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SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA
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ANALYSIS OF ALIPHATIC ALDEHYDES IN SOURCE EFFLUENTS AND IN
THE ATMOSPHERE

(Review)

A. P. ALTSHULLER, I. R. COHEN, M. E. MEYER AND A. F. WARTBURG JR.,
Anal. Chim. Acta, 25 (1961) 101-117

RELATIVE DATA OF CHEMICAL EQUILIBRIA GOVERNING THE SEPARATION OF
ZIRCONIUM FROM HAFNIUM

PARTS II AND III

(in French)

The chemical equilibria governing the separation of zirconium from hafnium are considered with particular reference to the solvent. The conditions of separation of a mixture of tributylphosphate, diluent and zirconium have been studied as well as the interaction of tributylphosphate and zirconium. The latter results in the formation of dibutylphosphate which has a strong complexing capacity for zirconium.

J. HURÉ, M. RASTOIX AND R. SAINT-JAMES, *Anal. Chim. Acta*, 25 (1961) 118-128

ON THE CONCENTRATION AND SEPARATION OF THE TRACE-ELEMENTS
Fe, Cu, Zn, Mn, Pb, Mo and Co

II. SOLVENT EXTRACTION

Extractions with acetylacetone and diethyldithiocarbamate are described. Through the successive application of these reagents the constituents of biological ashes are concentrated and separated into the groups: (1) MoO_4^{2-} , (2) Fe^{+3} , Cu^{+2} , (3) Mn^{+2} , (4) Zn^{+2} , (5) Pb^{+2} , (6) Co^{+3} and (7) Na^+ , K^+ , Ca^{+2} , Mg^{+2} , SO_4^{2-} , PO_4^{3-} .

P. C. VAN ERKELENS, *Anal. Chim. Acta*, 25 (1961) 129-135

INDIRECT OXIDIMETRIC DETERMINATION OF CERTAIN α -AMINO ACIDS
WITH VANADIUM(V)

A method for preparing standard vanadate solution using pure vanadium pentoxide as primary standard is described. The determination of certain α -amino acids by oxidation of their de-amination products with standard vanadate solution is studied.

S. P. RAO, H. S. RATHI AND J. N. GAUR, *Anal. Chim. Acta*, 25 (1961) 136-138

QUANTITATIVE ASPECTS OF THE OXIDATION OF ALIPHATIC ALCOHOLS BY POTASSIUM PERMANGANATE

I. METHANOL AND ETHANOL

The quantitative oxidation of methanol and ethanol by acidified potassium permanganate solution has been studied. Molybdate is superior to manganese(II) as the catalyst. In fairly dilute methanol solutions a large excess of permanganate oxidises the alcohol quantitatively to carbon dioxide. With ethanol, oxidation proceeds beyond the acetic acid stage but the further reaction is not stoichiometric.

J. SHARP, *Anal. Chim. Acta*, 25 (1961) 139-145

1,8-DIHYDROXYANTHRAQUINONE AS A REAGENT FOR BORIC ACID AND ITS USE IN THE ANALYSIS OF PHARMACEUTICAL GRADE GLASS

1,8-Dihydroxyanthraquinone is proposed as an organic reagent for boric acid. The color change obtained is more useful for the determination of boric acid than those with other reagents of the anthraquinone group. The method is applied to the determination of boric acid transfers from pharmaceutical grade glass.

R. RUGGIERI, *Anal. Chim. Acta*, 25 (1961) 145-149

APPLICATIONS OF THE CHELATOMETRY

VI. VOLUMETRIC DETERMINATION OF *vic*-DIOXIMES

(in French)

Vic-dioximes can be easily determined by precipitation with a nickel salt, excess of which is titrated with EDTA.

C. HENNART, *Anal. Chim. Acta*, 25 (1961) 150-152

A NEW REAGENT FOR THE DETECTION AND GRAVIMETRIC DETERMINATION OF SODIUM

5-Benzaminoanthraquinone-2-sulphonic acid is recommended as a reagent for the precipitation of sodium. It is the most sensitive precipitant for sodium yet proposed, being able to detect 5 μg of sodium at a limiting dilution of 1 in $4 \cdot 10^5$. The reagent is not selective and is unable to tolerate the presence of the other alkali metals and the ammonium ion. The use of the reagent for the gravimetric determination of 1.40-25.0 mg of sodium is described.

H. S. GOWDA AND W. I. STEPHEN, *Anal. Chim. Acta*, 25 (1961) 153-158

THERMOGRAVIMETRIC ANALYSIS OF METALLIC QUINALDATES

(in French)

Thermogravimetric analysis is used to determine the hydration of metallic quinaldates, as well as the thermal stability of the anhydrous quinaldates and of the water of hydration. Deductions are made with regard to structure by comparison with results previously obtained for oxinates and picolates.

G. THOMAS AND R. A. PÂRIS, *Anal. Chim. Acta*, 25 (1961) 159-165

A SENSITIVE NEW METHOD FOR THE DETERMINATION OF NITRITES AND NITROGEN DIOXIDE WITH 4-AMINOAZOBENZENE-1-NAPHTHYLAMINE

A sensitive method for the determination of nitrites is proposed. The method should also be applicable to the determination of nitrogen dioxide. The test consists of the reaction of 4-aminoazobenzene and 1-naphthylamine with nitrous acid to form the blue di-cation of 4-(*p*-phenylazophenylazo)-1-naphthylamine. Beer's law was obeyed from 0.5 to over 15 μg of nitrite ion per 15 ml of final solution. Spectrophotometrically it is possible to detect 1 part of nitrite ion in 60 million parts of solution.

E. SAWICKI AND J. L. NOE, *Anal. Chim. Acta*, 25 (1961) 166-169

A MODIFIED TRITIUM GAS COUNTING PROCEDURE

The WILZBACH one-step method for tritium analysis has been re-investigated because of difficulty in obtaining satisfactory results with the available catalysts. The important factors governing the conversion of tritium from an organic compound to the gaseous phase have been studied. Such factors include the use of zinc dust instead of zinc mesh for the reduction step, temperature of combustion, and the effect of variation in catalyst weight and sample size on conversion efficiency.

J. L. GARNETT, W. K. HANNAN AND S. W. LAW, *Anal. Chim. Acta*, 25 (1961) 170-175

p-(3-HYDROXY-3-PHENYLTRIAZENO)-PHENYLTRIMETHYLAMMONIUM CHLORIDE AS A NEW COLOUR REAGENT FOR CERTAIN METAL IONS

The synthesis and qualitative reactions of *p*-(3-hydroxy-3-phenyltriazeno)phenyltrimethylammonium chloride are described. The solubilising effect of the quarternary ammonium group is studied; this group is valuable for the conversion of organic precipitants to colorimetric reagents.

J. N. GAUR, N. K. MATHUR AND D. C. SANCHETI, *Anal. Chim. Acta*, 25 (1961) 176-178

THE DETERMINATION OF FLUORIDES IN NATURAL WATERS, WITH PARTICULAR REFERENCE TO SEA WATER

The chelate formed between lanthanum and alizarin complexone has been used as the basis of a method for the determination of fluoride in natural waters, with special reference to sea water. The fluoride complex formed with the reagent is developed rapidly at pH 4.50 by the addition of a single buffered reagent and is stable for several days. The fluoride complex is formed in 16% v/v acetone solution; the acetone stabilises the reagent and increases its sensitivity to 0.0018 $\mu\text{g}/\text{cm}^2$. Beer's law is followed up to ca. 25 μg of fluoride. The interference of inorganic ions present in natural waters has been investigated. Abnormally large amounts of aluminium interfere seriously, but can be removed by extraction as its oxinate in a continuous extractor. For sea water of chlorinity within the range 15 to 20‰ the salt error correction is constant and equal to 4.0%. The method showed a coefficient of variation of 0.3% with a sea water containing 1.37 μg of fluoride/ml.

R. GREENHALGH AND J. P. RILEY, *Anal. Chim. Acta*, 25 (1961) 179-188

DETERMINATION OF SILICA IN IRON ORE

A rapid and reliable routine method for determination of silica in iron ore has been developed and tested. The silica is converted to potassium fluosilicate by digestion with hydrofluoric acid, hydrochloric acid and potassium chloride and determined volumetrically.

Ö. GLASÖ AND G. PATZAUER, *Anal. Chim. Acta*, 25 (1961) 189-192

THE SEPARATION AND PHOTOMETRIC DETERMINATION OF CHROMIUM AND VANADIUM

A study was made on the extraction of hexavalent chromium from hydrochloric acid solutions with methyl isobutyl ketone. Quantitative extraction was accomplished from 3 *N* hydrochloric acid with 25 ml of solvent. Under these conditions, it was found that chromium could be extracted from vanadium. A procedure was developed for the colorimetric determination of chromium in the ketone phase and of vanadium in the aqueous phase. The analytical procedure was used to analyze standard steel samples for chromium and vanadium, and the results obtained by this method were found to agree with the accepted values.

S. A. KATZ, W. M. McNABB AND J. F. HAZEL, *Anal. Chim. Acta*, 25 (1961) 193-199

A NEW SPECIFIC TEST FOR ALUMINIUM

A new specific spot test for aluminium is described. The test is based on the demasking action of aluminium ion on calcium fluoride, and subsequent detection of the liberated calcium by glyoxal bis-(2-hydroxyanil).

E. JUNGREIS AND A. LERNER, *Anal. Chim. Acta*, 25 (1961) 199-201

APPLICATIONS OF THE CHELATOMETRY

XIV. VOLUMETRIC DETERMINATION OF *vic*-DIKETONES

(*Short Communication; in French*)

C. HENNART, *Anal. Chim. Acta*, 25 (1961) 201-202

POTENTIOMETRIC TITRATION OF THALLIUM(III) WITH CHROMIUM(II) SOLUTION

(*Short Communication*)

R. MAJUMDAR AND M. L. BHATNAGAR, *Anal. Chim. Acta*, 25 (1961) 203-204

Review

ANALYSIS OF ALIPHATIC ALDEHYDES IN SOURCE EFFLUENTS
AND IN THE ATMOSPHEREAUBREY P. ALTSHULLER, I. R. COHEN, MERLE E. MEYER AND
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Aldehydes have been identified in various combustion sources including automobile exhaust¹⁻⁴, diesel engine exhaust⁵, and incinerator effluents^{1,6-8}. Cooking of oils and varnishes in the paint and varnish industry and baking of molds in iron foundries are among the other sources producing significant amounts of aldehydes⁹. Several laboratory investigations have shown that aldehydes are major products from the photo-oxidation of olefin-nitrogen oxide mixtures^{10,11}.

Eye irritation appears to be a highly complex phenomena attributable to a number of gaseous species possibly adsorbed on aerosol particles. However, aldehydes such as formaldehyde and acrolein generally are considered to contribute a significant part of the total eye irritation^{10,11}. Upper respiratory and malodorant effects also have been attributed to aldehydes^{6,12}.

Irradiation of aldehydes has been reported to produce phytotoxicants which damage petunias and bean plants in the same way as do the products of irradiated hydrocarbon-nitrogen oxide mixtures¹¹. Such irradiated mixtures cause plant injury indistinguishable from the damage caused by the phytotoxicants in polluted air¹¹.

Since only formaldehyde and α,β -unsaturated aldehydes of all the aldehydes have been shown to be eye irritants in the part per million range, methods of analysis for these compounds are of particular interest. Plant damage effects may be produced by irradiation of saturated aldehydes, since α,β -unsaturated aldehydes do not photolyze significantly. Consequently, methods for total aliphatic aldehydes might be useful. It has been suggested that higher saturated aldehydes are highly unstable in air. While this conclusion is not supported by other laboratory evidence, it might be of interest to have a method for total higher saturated aldehydes. It is easier to cite needs for such methods than to develop sensitive and specific methods for particular compounds or subclasses of aldehydes. At present, colorimetric methods appear to be the most generally usable for analysis of combustion sources and the atmosphere. Polarographic procedures have been very useful in analyzing for aldehydes and formaldehyde in cool flame products and in some atmospheric work^{13,14}. Acrolein and crotonaldehyde have been analyzed in cool flame products and in products of the cooking of oils and the baking of molds in iron foundries^{9,13,15}. However, polarographic methods have not been widely applied to air pollution problems. In part this may

result from the lack of polarographic equipment in many laboratories. Gas chromatography and infrared spectroscopy certainly can be employed in analyzing for aldehydes in simplified systems^{10,11,16-18}, but are difficult to apply to aldehyde analysis in complex combustion effluents or the atmosphere.

METHODS OF ANALYSIS OF TOTAL ALDEHYDES

The method most widely used in practice to analyze for "aldehydes" is the bisulfite procedure^{19,20}. In this method an addition complex is formed between the aldehyde and the bisulfite compound, the excess bisulfite is destroyed, the addition compound decomposed, and the bisulfite ion released is titrated with standard iodine solution. Actually, both aldehydes and some ketones are determined by this method. Although formaldehyde, acetaldehyde and propionaldehyde may be efficiently collected and determined, it is generally more difficult to analyze quantitatively for ketones by this method^{21,22}. While the method has sufficient sensitivity for combustion effluent analysis, the limit of sensitivity often is being pressed in using the method to determine concentrations in the tenths of a p.p.m. range in the atmosphere^{19,21}.

All of the above factors tend to make the "aldehyde" concentrations determined by the bisulfite procedure somewhat uncertain. Obviously when large amounts of ketones exist in the combustion effluent or the atmosphere, the "aldehydes" determined will be higher than the true concentration of aldehydes. If significant amounts of ketones are present but the sampling is done at room temperatures or above, and at flow rates of 0.1 c.f.m. or higher, then some losses of ketones and of C₄ and higher aldehydes can result²¹. If only one or two impingers are used under these conditions even more serious losses may occur. Preferably, collection should be at about one liter per min into a series of three impingers placed in an ice bath. However, it also is possible that the degree of accuracy to be expected from the method in air pollution applications is insufficient to warrant all of the refinements mentioned. Whatever may be the limitations of this method, it is the only one which has been used in most investigations for aldehydes in combustion sources or in the atmosphere.

An argentimetric method using silver nitrate or silver oxide is quite specific for aldehydes, and it has some application for aldehyde analysis in combustion gases^{4,23}. The procedure, which involves titration of the silver salts with thiocyanate, is rather lengthy. The sensitivity is low, so the method is unlikely to be of any use in atmospheric analysis.

Another volumetric procedure which can be utilized involves oxidation of the aldehydes to the corresponding acids with hydrogen peroxide in *alkaline* medium^{4,24}. This method also is of limited sensitivity. It also may be applied to combustion gases but is of too low a sensitivity for atmospheric analysis.

An interesting polarographic method of aldehydes has been developed based on reduction of their semicarbazide derivatives¹⁴. Both aldehydes and ketones form such derivatives, but their half wave potentials are sufficiently different to permit a separate estimate of aldehydes and ketones. A small number of atmospheric measurements were made using this method. It might also be possible to determine the aldehydes directly in an appropriate electrolyte solution. Formaldehyde, α,β -unsaturated aldehydes, and C₂ and higher saturated aldehydes might be determined separately and then summed. Such a procedure should be applicable to combustion gases or other

effluents containing large amounts of aldehydes^{13,15}. Since deoxygenation usually is essential, volatile aldehydes may be swept out of solution. Also, in very complex combustion or atmospheric gas mixtures smearing out of the polarograms may effect adversely the quantitative accuracy.

Infrared spectroscopy is of only limited applicability to aldehyde analysis in complex gas mixtures. The carbon-hydrogen stretching vibration of aldehydes at $3.6\ \mu$ has been of some use for aldehyde analysis in combustion gases or the atmosphere. While irradiated mixtures of individual hydrocarbons and nitrogen oxides can be analyzed for aldehydes by infrared methods, infrared spectroscopy only can be used to obtain an estimate of total aldehydes in more complex mixtures²⁵. Of course, infrared analysis is very useful for other compounds, *i.e.*, olefins, ozone, organic nitrogen compounds, carbon monoxide, etc.

At present, it is difficult to determine aldehydes by gas chromatography in complex combustion mixtures^{16,18}. A number of the aldehydes are poorly resolved from other oxygenated compounds and hydrocarbons on the columns available¹⁸. Identification may often be possible, but accurate quantitative analysis is difficult^{16,18}. Although gas chromatography has a considerable potentiality for oxygenate analysis, much additional investigation is needed for its effective application to air pollution problems.

A combination of gas chromatography and infrared spectroscopy is much more effective than either method separately. Chromatographic separations which reduce the fractions going to the infrared instrument to two or three components make qualitative verification and quantitative analysis possible. Of course, sufficient material must be collected to be well above the sensitivity limits on the infrared equipment. Such a combination of techniques is powerful, but it is also expensive and time-consuming. While more detailed information may result, it also is possible that the essential composition data may be obtained more rapidly and inexpensively from other techniques such as colorimetric methods of analysis. This is not a criticism of such instrumental techniques. It is merely a suggestion that they are at present far more useful as research tools for a very limited number of highly detailed analyses, rather than as methods applicable to routine or semi-routine analysis.

A wide variety of color tests for aldehydes has been proposed. These tests are inadequately reviewed elsewhere^{22,26}. Only a few of these tests have adequate specificity, sensitivity and quantitative reproducibility and accuracy to warrant consideration as quantitative procedures for total aliphatic aldehydes. Only the limited number of such methods will be considered in the present discussion.

Schiff's reagent is one of the oldest reagents used for aldehydes^{26,27}. It is prepared from rosaniline hydrochloride (basic fuchsin) and sulfur dioxide. The quantitative procedure has many disadvantages. The sensitivity is less than that in the bisulfite method which makes it inadequate for atmospheric analysis²⁶. The sensitivities of the products of various aldehydes vary considerably²⁷. Furthermore, the linear relationship between absorbance and concentration is followed over only a narrow range of concentrations²⁷. The rate of color formation varies depending on the aldehyde considered²⁶. Finally, interference from sulfur dioxide, ethanol, acetone and similar compounds is appreciable²⁷. All of these factors combine to minimize the utility of this method in air pollution applications.

Reaction with 2,4-dinitrophenylhydrazine to form a colored product is a widely used procedure for identification of aldehydes and ketones²⁷. If it is used as an identi-

fication and analytical method following separation by column or paper chromatography, many individual aldehydes can be determined. However, such a procedure again is a research method satisfactory for the detailed analysis of a limited number of samples. Without separation it is difficult to analyze for the aliphatic aldehydes in the presence of ketones and aromatic aldehydes. In alkaline solution, aldehyde products show a rapid color fading²⁸. Analysis by difference initially and after several hours might possibly prove useful except that the fading is not complete and ketone derivatives also fade, although not as rapidly²⁸. Consequently, the method, without separation techniques, only gives a measure of total aliphatic and aromatic aldehydes and ketones present in a sample.

Recently a sensitive method for total aliphatic aldehydes has been presented²⁹. The method depends on the reaction of aldehydes with 3-methyl-2-benzothiazolone hydrazone to finally form a blue cationic dye. Filter paper, silica gel as well as colorimetric procedures for liquid samples have been developed²⁹. Aliphatic and aromatic ketones, aromatic aldehydes and phenols are reported not to interfere significantly. The method is sensitive enough to readily permit atmospheric analysis²⁹.

The problem with this method, as with many others, is the range of molar absorptivities for the products of various aldehydes. For example, the formaldehyde product has a molar adsorptivity of 65,000, the acetaldehyde product, 51,000, the 2-methylpropanal product, 23,000 and the acrolein product 23,000, all at an adsorption maximum near 670 $m\mu$ ²⁹. In a complex mixture of unknown composition, the aldehyde content even if expressed in terms of formaldehyde is subject to significant uncertainty. This is a frequent problem in colorimetric analysis for whole classes of compounds. Overall, this method appears to have possibilities.

METHODS OF ANALYSIS FOR FORMALDEHYDE

Several volumetric methods have some degree of specificity for formaldehyde. These include the potassium cyanide, hydrogen peroxide (mild oxidation) and ammonia procedures²⁷. Of these three methods, the potassium cyanide method appears to be the most specific and it has been used to analyze for formaldehyde in automobile exhaust gases⁴. This method involves the reaction of the cyanide with the formaldehyde to form the cyanohydrin, conversion of the excess cyanide to silver cyanide with a known excess quantity of standard silver nitrate solution and finally the titration of the excess silver nitrate with thiocyanate^{4,23}. The method has the limited sensitivity of the usual volumetric procedure, and it would be very difficult to apply it to the atmospheric analysis of formaldehyde.

Formaldehyde has been analyzed for polarographically in a number of simple mixtures^{30,31} and in cool flame combustion products^{13,15}. Polarograph determinations of formaldehyde have been reported to agree well with analyses made simultaneously by colorimetric methods³⁰. It has been shown that polarographic analysis for formaldehyde should not be interfered with by acrolein, crotonaldehyde, acetaldehyde, propionaldehyde, methanol, formic acid, phenol, hydrogen peroxide or organic hydroperoxides^{13,30,31}. No analyses appear to have been made for formaldehyde by polarographic methods on combustion effluents from automobiles or incinerators or on samples collected from urban atmospheres.

The infrared spectrum of formaldehyde is not particularly characteristic. In com-

plex mixtures it is not possible to distinguish the C-H stretch or the carbonyl bond of formaldehyde from the overall absorption due to aldehyde and carbonyl compounds. Consequently, infrared spectroscopy alone does not appear to be useful for the identification and analysis of formaldehyde in combustion or atmospheric gas.

Considerable difficulty has been experienced in identifying formaldehyde by gas chromatography^{16,18}. The compound or its polymer appears to be either irreversibly absorbed or covered by the water band in a number of attempts to identify it. Recently, it has been reported that formaldehyde has been detected and analyzed on a firebrick column coated with a surfactant³². Five and six carbon hydrocarbons probably would interfere in combustion or atmospheric mixtures even with use of multiple stage gas chromatography.

Several colorimetric procedures are available for the analysis of formaldehyde. Some of these procedures are both sensitive and specific enough to use for both complex combustion and atmospheric gases.

One of the earlier colorimetric methods used Schiff's reagent in acidic media²⁷. Other aldehydes form colored products which fade much more rapidly than does the formaldehyde product. The formaldehyde product also fades slowly so the absorbance must be read shortly after acidification²². This procedure is not very sensitive, nor highly reproducible, and the procedure is subject to several interferences^{22,27}. However, it is satisfactory for determining formaldehyde in some mixtures.

Among the reagents used in the analysis of formaldehyde, chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid) has a very high sensitivity²². This method has been widely used for the analysis of formaldehyde³³⁻³⁵. When the sulfuric acid content used is above 85% the product formed by chromotropic acid with formaldehyde is very stable, has a high color intensity, and obeys Beer's Law over a wide concentration range^{34,35}. This procedure is both simple and rapid in its application to the analysis of formaldehyde either as a combustion effluent or as an atmospheric pollutant³⁵.

The interference situation for the chromotropic acid method has been investigated in detail. Such studies have not been made for most of the other analytical methods for aldehydes. It has been shown that mixtures of saturated aldehydes, ketones, methanol, ethanol, nitrogen dioxide and sulfites with formaldehyde do not affect the analysis by the chromotropic acid procedure³³⁻³⁵. Unsaturated aldehydes such as acrolein or crotonaldehyde, even if present in equal amounts with formaldehyde, interfere only slightly in this analysis^{34,35}. Three carbon and higher straight-chain alcohols interfere slightly if present in large excess³⁵. Branched chain alcohols interfere significantly if present in excess³⁵. Olefins react with formaldehyde as do alcohols via the Prins reaction. Four carbon and higher olefins will interfere, but in gas mixtures, this interference can be minimized by appropriate collection conditions³⁵. Aromatic hydrocarbons and phenols in excess of the formaldehyde concentration can interfere significantly³⁵. The interference of aromatic hydrocarbons can be minimized by the proper collection medium, but phenols in excess will interfere generally with the analysis of formaldehyde by the chromotropic acid method³⁵. It will be shown later in this work that, despite these interferences, the chromotropic acid method appears adequate for analysis of formaldehyde in situations of air pollution importance.

Formaldehyde can be determined as the formazan or its anion formed by reacting the aldehyde with a hydrazine, and oxidizing the product. Further reaction produces

the formazan which can be converted to a highly colored anion. Phenylhydrazine has been used as the hydrazine and potassium ferricyanide as the oxidizing agent. The earlier procedures produced rather unstable products^{30,36}. Other aldehydes interfered. An improved modification was reported which has been used to analyze for formaldehyde in automobile exhaust³⁷. Recently a modification has been published which used 2-hydrazinobenzothiazole instead of phenylhydrazine as the reagent³⁸. The product formed appears to be more intensely colored and more stable than the product formed in the phenylhydrazine procedures. In contrast to the chromotropic acid procedures which determines formaldehyde and substances which hydrolyze to formaldehyde in sulfuric acid, the hydrazine procedures are claimed to determine only formaldehyde³⁷.

METHODS OF ANALYSIS FOR CONJUGATED UNSATURATED ALDEHYDES

Only a few chemical procedures have any specificity for unsaturated aldehydes such as acrolein, α -methylacrolein or crotonaldehyde. Unsaturated aldehydes as a group may be determined by bromination²⁷, if other easily brominated species such as olefins and phenols are absent from the sample being analyzed. Such restrictions make bromination procedures of little use in air pollution applications. Unsaturated aldehydes, as well as other types of unsaturated oxygenates, can be analyzed by addition of excess dodecanethiol and titration of the excess mercaptan iodometrically²⁷.

The infrared bands characteristic of unsaturated aldehydes are overlapped by bands due to water vapor, other types of carbonyl compounds and some types of olefins. While it is possible to analyze for acrolein and other α,β -unsaturated aldehydes in photolyzed mixtures of single diolefins with nitrogen oxides¹⁰, it is not possible to determine unsaturated aldehydes by infrared spectroscopy in complex mixtures.

Unsaturated aldehydes can be analyzed in cool flame products of single hydrocarbons by polarographic methods^{13,15}. Since the half-wave potentials of acrolein, α -methylacrolein and crotonaldehyde are quite close to each other, it is doubtful that individual unsaturated aldehydes can be determined without preliminary separations. This is well realized by investigators using polarographic techniques. With preliminary separation as the 2,4-dinitrophenylhydrazones, acrolein and crotonaldehyde have been individually determined in cool flame products¹⁵. The applications to cool flame work involved mg quantities of aldehydes.

The polarographic method also has been applied to determine acrolein (and crotonaldehyde, if present) in mold burning in iron foundries and in cooking of oils and varnishes in the paint and varnish industry⁹. In these applications to situations in which the acrolein concentration was less than 1 p.p.m., the sampling and transfer procedure used was elaborate and time-consuming⁹.

Acrolein, crotonaldehyde, and possibly α -methylacrolein have been identified in automobile exhaust gases and cool flame products by means of gas chromatography¹⁸. Complete or nearly complete resolution of the unsaturated aldehydes from other oxygenated species is difficult to obtain¹⁸. Higher molecular weight aliphatic and aromatic hydrocarbons also interfere. Again, a combination of gas chromatography and infrared methods should make analysis possible.

Three colorimetric methods have been used for the analysis of acrolein. Tryptophan³⁹, phloroglucinol⁴⁰, and 4-hexylresorcinol^{41,42} are used as color producing reagents in these methods. The tryptophan and phloroglucinol methods are insuffi-

ciently sensitive for analysis of acrolein in the p.p.m. range and below⁴². Appreciable interference results in these two procedures from the presence of excess amounts of other aldehydes, particularly formaldehyde, as well as from nitrogen dioxide and nitrates⁴². The 4-hexylresorcinol method has been applied to the analysis of raw, diluted and irradiated automobile exhaust gases, and also to a wide variety of liquid mixtures⁴². No significant interferences with the analysis of acrolein by the 4-hexylresorcinol method have been found in the applications investigated. The sensitivity of this procedure is such that less than one p.p.h.m. of acrolein readily can be detected⁴². The absorbance is linear with concentration of acrolein over a wide range⁴².

Crotonaldehyde can also be analyzed using 4-hexylresorcinol method⁴³. In contrast to the acrolein which forms a blue product with an absorption maximum at 605 m μ , crotonaldehyde forms a product with its stronger absorption maxima at 385 and 345 m μ . These bands may be used to analyze for crotonaldehyde in the presence of most aliphatic hydrocarbons, oxygenates and aromatics⁴³. However, unsaturated compounds including α -methylacrolein, 3-buten-2-one, furfural, and 1,3-pentadiene interfere somewhat if present in excess⁴³. Acrolein interferes significantly in small quantities but the 605-m μ peak can be used to correct for the acrolein. More serious is the interference of nitrogen dioxide in the ultraviolet⁴³. This interference restricts the application of the crotonaldehyde procedure to systems containing small or negligible amounts of nitrogen dioxide.

α -Methylacrolein and furfural also can be identified, but not quantitatively analyzed by the 4-hexylresorcinol method. α -Methylacrolein has an absorption maximum at 480 m μ , while furfural has maxima⁴² at 650, 550 and 445 m μ .

METHODS OF ANALYSIS FOR TOTAL HIGHER ALDEHYDES

No volumetric or infrared method is particularly applicable to the analysis of total higher aldehydes above formaldehyde. Polarographic procedures might be used. The available data indicate that unsaturated aldehydes, acetaldehyde and propanal and higher aldehydes might be determined separately and summed together^{13,15,31}. Gas chromatographic techniques can be applied with the serious limitations discussed previously.

No colorimetric method is available for the direct determination of total higher aldehydes. Very few of the reactions which form colored products occur for higher aldehydes and not for formaldehyde. A sodium nitroprusside-secondary amine type reaction might have possibilities^{22,26,44}. Recently, it has been shown that *p*-nitrobenzene-diazonium fluoborate in a phosphoric acid-2-methoxyethanol solvent medium reacts with propanal, acrolein and higher aldehydes, but not significantly with formaldehyde and acetaldehyde⁴⁵. However, this reagent also reacts with ketones other than acetone.

The remaining alternative is to use a colorimetric method specific for formaldehyde, another method specific for total aldehydes, and subtract the values obtained to give total higher aldehydes. Obviously, the limitations in the two separate methods will make the difference in values only approximate. For example, assume that the chromotropic acid³³⁻³⁵ or 2-hydrazinothiazole method³⁸ is used to determine formaldehyde, while the 3-methyl-2-benzothiazole method²⁹ is used for total aldehydes. Assume further that the distribution of atmospheric aldehydes actually is as follows: formaldehyde, 50 p.p.h.m.; acetaldehyde, 10 p.p.h.m.; propanal, 10 p.p.h.m.; butanal,

5 p.p.h.m.; 2-methylpropanal, 5 p.p.h.m.; pentanals, 5 p.p.h.m.; hexanals and higher aldehydes, 5 p.p.h.m.; acrolein, 5 p.p.h.m.; crotonaldehyde, α -methylacrolein, glyoxal, 5 p.p.h.m. Using the absorptivities given for individual aldehydes, the 3-methyl-2-benzothiazolone procedure gives a concentration of 83 p.p.h.m. for "total aldehydes as formaldehyde". If the formaldehyde method used measures the actual formaldehyde concentration as 50 p.p.h.m., then the apparent total higher aldehyde content will be 33 p.p.h.m. rather than 50 p.p.h.m. This 33% error is the result of the spread of three-fold in the absorptivities for individual aldehydes. This type of problem often will arise in the application of a colorimetric class analysis method to a complex mixture in air pollution studies.

METHODS OF ANALYSIS FOR GLYOXALS

Volumetric, infrared and polarographic methods for glyoxal are either insufficiently sensitive, specific or accurate for the analysis of glyoxal. Gas chromatography may be applicable, but experimental data are not available.

A highly sensitive and apparently a very specific method for glyoxal has been reported based on its reaction with 2,3-diamino-phenazine to form pyrazino(*b*)-phenazine, an intensely blue-colored product⁴⁶. Methylglyoxal also reacts but a much less intensely colored product is formed. This method even permits the analysis of glyoxal and methylglyoxal in the presence of diketones and hydroxyalkanals⁴⁶. A less sensitive and specific procedure might be developed from the reaction of glyoxal with phenylhydrazine and potassium ferricyanide in acidic media to form a formazan absorbing at 375 m μ with a molar absorptivity⁴⁷ of 34,800. A sensitive fluorescent spot test for glyoxal also has been described recently based on the fluorescence products formed when glyoxal reacts with several reagents including 2-hydrazinobenzothiazole⁴⁸.

PREVIOUS EXPERIMENTAL RESULTS ON SOURCE EFFLUENTS

Data are available on "aldehyde" concentrations from many sources including burning fuel gas, fuel oil, ovens, furnaces, steam boilers, incinerators and automobile exhaust¹⁻⁸. Most of the data have been obtained using the bisulfite method and the values represent carbonyl content. The results are summarized in Table I. The values given can only be taken as roughly indicating the concentrations produced by the various combustion devices. Different devices of the same general type operating under differing conditions will give a fairly wide range of values. This is shown by the data available on domestic incinerators and automobile exhaust effluents. The results for the automobile must also be defined in more exact terms for the driving cycle, general engine and ignition conditions and for the fuel used. In one investigation aldehyde content was found to increase from 70 to 96 p.p.m. under cruising conditions as speed was increased from 15 to 60 MPH.

It is difficult to say how much of the so-called aldehyde reported in many of these investigations is ketone, which is also determined by the bisulfite method used. In one of the domestic incinerator studies made, acetone was determined separately by infrared methods as something under 260 $\mu\text{g/l}$, while the total carbonyl content ranged from 180 to 1960 $\mu\text{g/l}$ in various runs⁷. The carbonyl content, as measured by three methods (hydroxylamine hydrochloride, sodium bisulfite, and 2,4-dinitrophenylhydrazine methods) on automobile exhaust, and the aldehyde content (alkaline

hydrogen peroxide and argentimetric methods) did not differ significantly⁴. Furthermore, the methyl ketone content was very small. Whether higher aliphatic aldehydes have been collected effectively in many of these investigations also is difficult to ascertain.

TABLE I
ALDEHYDE CONTENTS OF SOURCE EFFLUENT GASES

Source	Conc. of aldehydes, as p.p.m. or $\mu\text{g/l}$
range oven ⁶	11 p.p.m.
water heater ⁶ , 100 gallon	8 p.p.m.
floor furnace ⁶	3 p.p.m.
steam boiler ⁶ , low fire	5 p.p.m.
fuel gas combustion ¹	60 $\mu\text{g/l}$
fuel oil combustion ¹	75 $\mu\text{g/l}$
domestic incinerator-Timmings ¹	125 $\mu\text{g/l}$
domestic incinerator-paper ¹	44 $\mu\text{g/l}$
domestic incinerator-mixed change ⁷	180-1960 $\mu\text{g/l}$
municipal incinerator ¹	60 $\mu\text{g/l}$
automobile exhaust - idle ¹⁻³	100 $\mu\text{g/l}$, 88 p.p.m., 60 p.p.m.
- cruise ¹⁻⁴	200 $\mu\text{g/l}$, 264 p.p.m., 140 p.p.m., 70-96 p.p.m.
- accel. ²	1369 p.p.m.
- decel. ^{2,3}	193 p.p.m., 190 p.p.m.
diesel engine ⁵	7 p.p.m.

The formaldehyde concentration in a multiple-chambered experimental incinerator was only in the 0.1 to 1 p.p.m. range when a high volatile fuel was used⁸. Formaldehyde was determined by direct sampling into sulfuric acid containing 0.1% chromotropic acid.

The formaldehyde content of auto exhaust was found to range from 29 to 43 p.p.m. for 15, 40 and 60 MPH cruise conditions⁴. The phenylhydrazine and potassium cyanide methods were used for analysis of the formaldehyde. The formaldehyde was just under half of the total aldehyde content in this investigation⁴.

An analysis indicating 3 p.p.m. of acrolein in automobile exhaust has been reported¹. No experimental details are available. Polarographic determinations of acrolein produced in mold pouring and varnish cooking operation⁹ were reported as 0.5 and 0.4 p.p.m. The corresponding total aldehydes⁹ (as formaldehyde) were reported to be 3.3 and 2.0 p.p.m.

This brief survey is not meant to represent an exhaustive review of the literature. The data does point out the relatively large emissions of aldehydes per unit of volume from automobiles and domestic incinerators. More exhaustive and specific analyses for total and individual aldehydes on some of the sources in Table I would be desirable.

PREVIOUS EXPERIMENTAL RESULTS ON THE ATMOSPHERE

A considerable number of measurements of atmospheric "aldehyde" content by the bisulfite method have been reported^{6,49-54}. Concentrations exceeding 1 p.p.m. have been reported, with a number of maximum values between 0.5 and 1 p.p.m. Average

aldehyde values in the Los Angeles basin are in the 0.1 to 0.5 p.p.m. range⁶; however, average values in most localities are around 0.05 p.p.h.m.^{49,50}. Many of the older data have been tabulated elsewhere⁴⁹.

Data also is available on three more recent studies in Houston⁵¹ and El Paso, Texas⁵² and in Southern Ontario⁵³. In the Houston⁵¹ study most of the concentrations were in the 0–0.1 p.p.m. range with one value of 0.3 and another of 1.3 p.p.m. In the El Paso⁵² study a considerable number of daily measurements were made at three stations over two periods of several months each. The average aldehyde values (again by the bisulfite method) were around 0.05 p.p.m. However, maximum values between 0.4 and 0.5 p.p.m. were obtained. A more detailed analysis of the data shows that while most of the values were in the 0.00 to 0.05 range, 10 or 20% of the values are in the 0.1 to 0.2 p.p.m. range⁵². In the Southern Ontario studies it was reported that most of the readings were below 0.70 p.p.m. but that peaks as high as 3 p.p.m. were measured⁵³. A study in the Southern Ontario⁵⁴ area 7 years before this work gave an average value of 0.2 p.p.m. and a maximum value of 0.75 p.p.m.

A small number of determinations of aldehydes as formaldehyde and separately of ketones have been made by polarographic reduction of the semicarbazones¹⁵. One measurement made on the Los Angeles atmosphere gave 0.6 p.p.m. aldehydes and 0.4 p.p.m. ketones as acetone. Later measurements on solutions several days old which may have lost their aldehyde content gave 0.1–0.2 p.p.m. as acetone¹⁵.

With a few exceptions the number of atmospheric "aldehyde" measurements even by the bisulfite method at various localities is small. The measurements made thus far show that there are times in a number of cities during which the "aldehyde" content may reach 0.5 p.p.m. or higher. Such concentrations are comparable with the sulfur dioxide, nitric oxide, and hydrocarbon contents in many localities. Since the aldehydes have been related to many deleterious effects, more measurements of total carbonyls, total aldehydes, formaldehyde and unsaturated aldehydes in urban atmospheres are both desirable and necessary.

EXPERIMENTAL RESULTS ON THE ANALYSIS OF FORMALDEHYDE IN AUTOMOBILE EXHAUST EFFLUENT

An investigation has been made in our laboratories of the applicability of various modifications of the chromotropic acid method to the analysis of formaldehyde in the automobile exhaust. The automobile was run on a 30 MPH cruise. The chromotropic acid method was chosen because of its good sensitivity and ease of application. Most of the sampling was done directly into evacuated 2-l glass flasks. Some samples were collected in aluminized scotchpak bags, others directly into impingers and bubblers.

No formaldehyde could be detected in exhaust gas samples collected into aluminized scotchpak bags, and then transferred to evacuated flasks containing 1% aqueous sodium bisulfite solutions. Essentially no formaldehyde could be determined in samples collected in evacuated flasks, bubblers or impingers containing 0.1% chromotropic acid in sulfuric acid. Finally, when the samples were collected in empty flasks to which 1% aqueous sodium bisulfite solution was added later, no formaldehyde could be recovered.

Appreciable amounts of formaldehyde can be determined in samples collected directly into evacuated flasks containing water, 1 or 40% bisulfite solutions or into

TABLE II

FORMALDEHYDE IN AUTOMOBILE EXHAUST AS DETERMINED BY VARIOUS CHROMOTROPIC ACID PROCEDURES

Collection solution	Reaction time outside flask, in min	Formaldehyde in p.p.m. Time period between sampling and removal of sample from flask, in min			
		5	10	15	20
water	<5	21	15	<1	<1
water	60	24	19	<1	<1
1% aqueous bisulfite	<5	21	15	10	6
40% aqueous bisulfite	<5	21	14	13	12
40% aqueous bisulfite	60	27	27	26	25

TABLE III

FORMALDEHYDE IN AUTOMOBILE EXHAUST AS DETERMINED BY CHROMOTROPIC ACID METHOD AFTER COLLECTION IN 40% BISULFITE SOLUTION

Reaction time outside flask, in min	Formaldehyde in p.p.m. Time period between sampling and removal of sample from flask, in min			
	1	15	30	60
5	24	16	15	16
30	26	23	21	20
60	26	22	23	24
120	28	23	22	23

impingers containing the same solutions. Very small amounts of formaldehyde can be detected from samples passed through a bubbler containing 1% bisulfite solution. The samples passed through the impingers containing 1 or 40% bisulfite solution analyzed to give only 20 to 40% of the formaldehyde content found for equivalent samples collected in evacuated flasks containing the same solutions.

The results in p.p.m. by volume of formaldehyde under different collection and reaction conditions are shown in Tables II and III. These data indicate that it is desirable to remove the aliquot for analysis from the flask as rapidly as practical, and that a waiting period of about 1 h is desirable before chromotropic acid is added to the aqueous aliquot. If 40% bisulfite solution is used and the aliquot is held for as much as 1 h before analysis, only a 10 to 20% decrease in concentration will result even if the aliquot for analysis remains in the flask for 1 h.

Extrapolation of the present data to zero time in flask after collection, with a 60-min holding time before analysis, would result in a formaldehyde concentration of just under 30 p.p.m. In previous work an average formaldehyde concentration of 29 p.p.m. (range 25–33 p.p.m.) at 15 MPH cruise and 39 p.p.m. (range 28–51 p.p.m.) at 40 MPH cruise were reported. A concentration of about 30 p.p.m. at 30 MPH cruise certainly is in the same range. Considering the difference in fuels and operating conditions (engine dynamometer *versus* automobile on chassis dynamometer) the general agreement is very good.

The loss of formaldehyde found when sampling into a scotchpak bag can be explained without difficulty. Hot exhaust is being collected and as condensation of water occurs, formaldehyde is carried down with it. Any formaldehyde remaining

may be lost by adsorption on the liquid film formed on the surface of the bag. The loss of formaldehyde in dry glass flasks further indicates the great difficulty of sampling into a dry container. It is much more difficult to understand the essentially complete loss in the glass flasks. It might be thought that losses on the walls would be recovered when the absorbing solution is added. However, these results were obtained on four different flask samples. In all of these runs the aliquot for analysis was removed less than 5 min after addition of the 1% bisulfite solution. Irreversible reactions of formaldehyde in the dry flask must remove it permanently from the gas and surface phases.

The inability to detect formaldehyde when sampling into flasks, bubblers or impingers containing 0.1% chromotropic acid in sulfuric acid must be attributed to loss of formaldehyde through reaction with interfering substances, particularly aromatic species. The lower formaldehyde concentrations found when sampling into bisulfite solutions in bubblers or impingers rather than evacuated flasks are somewhat more troublesome to explain. It may be that interfering materials are collected by the bubblers or impingers containing bisulfite solution more effectively than by the bisulfite solution in the flask. Support for this argument is found in the lower formaldehyde concentrations obtained even for samples collected in flasks, if the aliquot for analysis is not removed immediately. Apparently, the formaldehyde is collected quite rapidly and efficiently by the bisulfite solution in the flasks, but the interfering substances are absorbed by the aqueous bisulfite solution more slowly. The decrease in formaldehyde is not likely to be the result of polymerization or volatilization of formaldehyde. Samples removed from the flasks and allowed to stand in test tubes actually analyze to give higher formaldehyde concentrations than those analyzed immediately. The latter result may be due to hydrolysis of combined formaldehyde, since the aqueous solutions are acidic. Perhaps, part of the increase is due to the hydrolysis of formals produced in the combustion process. Some evidence for their existence is available from gas chromatographic studies of automobile exhaust from pure hydrocarbon combustion¹⁸.

Acrolein has been found in automobile exhaust up to concentrations of 9 p.p.m., Table IV. The concentration found for a given automobile may be very sensitive to engine or carburetor adjustments. The same automobile which produced 7-9 p.p.m. during a number of runs produced only about 1 p.p.m. after carburetor adjustment. After a running of the same automobile a number of additional hours, the acrolein concentration climbed up to 4 p.p.m. It is possible that both formaldehyde and acrolein are very sensitive indices of minor changes in automobile operating conditions.

TABLE IV
ANALYSES FOR ACROLEIN IN AUTOMOBILE EXHAUST

Type of sample	Collection method	Conc. of acrolein, p.p.m. by volume
cruise auto exhaust ^a	bubblers	8.3
cruise auto exhaust ^a	plastic bag ^b	8.7
decel. (coasting) exhaust	plastic bag ^b	7.0
cruise and decel. exhaust	bubblers	7.0

^a 30 MPH cruise samples collected at about the same time

^b aluminized scotchpak bag

ANALYSIS OF DILUTED AUTOMOBILE EXHAUST

A number of analyses of the formaldehyde concentration were made after dilution but before irradiation. Samples were collected directly into impingers or bubblers from a tap in the dilute exhaust line going into an irradiation chamber. Impingers were used for collecting the formaldehyde in 0.1% chromotropic acid in sulfuric acid³⁵, while bubblers were used when collecting samples in water^{34,35} or 2-hydrazino-benzothiazole reagent³⁸.

Typical results for formaldehyde using the three collecting solutions were as follows: (1) 0.1% chromotropic acid in sulfuric acid, 8 p.p.h.m.; (2) 0.25% aqueous 2-hydrazinobenzothiazole solution, 46 p.p.h.m.; (3) water, 60 p.p.h.m. Again, as found for exhaust directly from the engine, collection of diluted exhaust in sulfuric acid gave extremely low results for the formaldehyde.

Some preliminary results on formaldehyde were made on even more highly diluted automobile exhaust by collection in sulfuric acid containing 0.1% chromotropic acid. Comparison of the formaldehyde contents obtained by this procedure with those obtained by collection in aqueous solutions indicates more satisfactory results in the more diluted gas mixture. However, direct collection of automobile exhaust gases in sulfuric acid medium usually gave quite unsatisfactory results and should be avoided.

Higher formaldehyde values are found by analyzing with chromotropic acid reagent after collection of the formaldehyde in aqueous media than when analysis is made subsequent to collection in 2-hydrazinobenzothiazole reagent. The difference observed could be due to interferences or to the two methods measuring different species.

Both alternatives are possibilities. However, all of the experimental data available on the chromotropic acid method indicate that almost all of the possible major interferences tend to reduce the measured formaldehyde content. No significant interferences have been reported for the 2-hydrazinobenzothiazole method³⁸. In both methods some higher aldehydes and diketones give a small response which might increase the observed absorbance, but by only a few percent at most. The other alternative is that the chromotropic acid procedure is measuring formaldehyde and also a significant quantity of formals while the 2-hydrazinobenzothiazole only measures formaldehyde. Some evidence for such a possibility has been discussed in the previous section. Further investigation will be necessary to interpret these differences with any certainty.

Acrolein has been determined on the same runs for which formaldehyde data are available⁴². The acrolein concentration in the diluted non-irradiated automobile exhaust was in the 4 to 6 p.p.h.m. range. Consequently, the acrolein concentration was about 10% of the formaldehyde concentration.

ANALYSIS OF DILUTED, IRRADIATED AUTOMOBILE EXHAUST

A larger number of analyses have been made on irradiated exhaust for formaldehyde and acrolein. Most of the determinations for formaldehyde have been made by various of the chromotropic acid procedures^{34,35}. However, a number of determinations have been made using both collection into sulfuric acid, water or bisulfite solution with the chromotropic acid method and collection in 2-hydrazinobenzothiazole reagent³⁸.

Most of determinations were made on samples pulled out of a mylar bag filled with

the irradiated exhaust. Formaldehyde diluted in air was moderately stable in a mylar bag. The following absorbances were obtained when 5-l samples were analyzed by the chromotropic acid method after the formaldehyde had remained in the bag for some time: 0.5 h, 0.88; 2.5 h, 0.89; 20.5 h, 0.87; 24 h, 0.84. However, actual irradiated exhaust samples lost formaldehyde from the gas phase somewhat rapidly. Two different runs showed that a 5 to 10% loss of formaldehyde occurred (probably to the walls) after the sample remained in the bag for about 2 h.

This loss would not invalidate the main results obtained in the comparative determinations. Furthermore, the duplicate determinations by one of the procedures made in two of the runs allow corrections to be made for the losses experienced. In addition to the bag runs, several determinations were made at the same or nearly the same times on samples taken into bubblers directly from the irradiation chamber.

TABLE V
FORMALDEHYDE ANALYSIS ON DILUTED, IRRADIATED EXHAUST

Run	Analytical method	Collection medium ^a	Formaldehyde conc. p.p.m. by volume
1	chromotropic acid	water	2.7 ^b
	2-hydrazinobenzothiazole	0.25% aq. 2-HTB	2.1
	chromotropic acid	water	2.5
2	chromotropic acid	0.1% chromotropic acid in H ₂ SO ₄	1.7
	chromotropic acid	0.1% chromotropic acid in H ₂ SO ₄	2.1
	2-hydrazinobenzothiazole	0.25% aq. 2-HTB	2.3
	chromotropic acid	water	2.5
3	chromotropic acid	water	2.5
	2-hydrazinobenzothiazole	0.25% aq. 2-HTB	2.1
4	chromotropic acid	0.1% chromotropic acid in H ₂ SO ₄	2.3
	2-hydrazinobenzothiazole	0.25% aq. 2-HTB	2.6
	chromotropic acid	water	3.1

^a Samples of raw exhaust, diluted 100:1 and irradiated were pulled out of irradiation chamber into a mylar bag and then pulled through the collecting medium contained in a bubbler or impinger.

^b Four formaldehyde analyses by this procedure on samples collected in bubblers directly from chamber averaged 2.9 ± 0.2 (σ) p.p.m.

Four sets of determinations on a mylar bag sample are shown in Table V. The determinations from all of the runs were averaged and the analyses obtained by the 2-hydrazinobenzothiazole proved to give 0.85 of the formaldehyde concentration obtained by sampling into water or bisulfite solution and then reacting with chromotropic acid reagent. The direct sampling and analysis with 0.1% chromotropic acid reagent in sulfuric acid gave 0.75 of the formaldehyde concentration obtained by sampling into water or bisulfite solution and then reacting with chromotropic acid reagent. Consequently, the very simple and sensitive procedure of directly sampling and analyzing in 0.1% chromotropic acid in sulfuric acid may be applicable in atmospheric analysis work. It should be mentioned that the fuels used contained 40% aromatic hydrocarbons. Thus the interference situation in the irradiated system used actually may be worse than in the atmosphere for this chromotropic acid procedure³⁵. The previous discussions probably apply to the lower results obtained for formaldehyde content by the 2-hydrazinobenzothiazole method compared to the aqueous sam-

pling procedure with the chromotropic method on the irradiated samples. However, little is known about the interference problems in the 2-hydrazinobenzothiazole method in the very complicated diluted, irradiated automobile exhaust systems.

Acrolein determinations were made on the same runs⁴². While the formaldehyde determinations using aqueous collecting medium and the chromotropic acid method averaged 2.7 p.p.m., the acrolein concentration for the same runs averaged 0.18 p.p.m.

The formaldehyde found in the exhaust diluted 100:1, 0.6 p.p.m., is about 22% of the formaldehyde found in the corresponding irradiated exhaust. The acrolein in the diluted, non-irradiated exhaust constitutes about one-third of the acrolein found in the irradiated exhaust. Consequently, most of these two aldehydes are produced by photooxidation reactions, but the contribution directly from the automobile is significant. These results should be generalized with caution. The data is obtained by burning special experimental gasolines in a single automobile mounted on a chassis dynamometer, diluting the exhaust with purified air, and irradiating the mixture in an aluminium chamber with fluorescent lamps through mylar windows⁵⁵.

CONCLUSION

The previous discussion indicates that there are available many potential methods for the analysis of aldehydes in combustion sources and in the atmosphere. Several of the volumetric and colorimetric methods have been applied successfully to air pollution situations. More colorimetric methods for certain aldehyde subclasses would be desirable. Polarographic procedures, perhaps along with other electrometric methods, appear to have a certain real range of applicability. Gas chromatography can be applied to many somewhat simplified systems. Better column materials and detectors should increase the applicability of gas chromatography to aldehyde analysis. Infrared and mass spectrometric methods have some applicability in aldehyde analysis in simple laboratory systems. However, they are much more powerful tools when applied in combination with other methods.

Of the methods discussed, a few of the volumetric techniques and a number of the colorimetric procedures for aldehydes have real applicability to rapid analysis of many samples in the field or laboratory. The others, with the possible exception of some polarographic or electrometric techniques, are essentially research methods. These methods alone or in combination can provide a great deal of valuable detailed information on a few samples, at a rather high cost in personnel and equipment per sample.

The chromotropic acid method employing collection in aqueous solution is the simplest, most rapid and generally convenient procedure for analysis of raw, diluted and irradiated automobile exhaust and numerous other applications. The hydrazinobenzothiazole method is much more time-consuming, and the sensitivity is less than twice that of the chromotropic acid procedure. Direct collection in 0.1% chromotropic acid in sulfuric acid provides an extremely rapid and simple procedure. Since no dilution is involved, the method is considerably more sensitive than the hydrazinobenzothiazole method. However, the procedure is not applicable to some types of combustion source analysis. Direct collection in chromotropic acid does appear usable for atmospheric or irradiation chamber analysis.

The 4-hexylresorcinol method is highly sensitive. It is applicable to the analysis of raw, diluted and irradiated automobile exhaust and other gases and liquid phase analysis for acrolein.

Despite some limitations in our analytical methodology, we have many methods available which have rarely, if ever, been applied to the analysis of aldehydes in air pollution situations. Much more information can and should be obtained with existing techniques on all types of combustion and pyrolysis source samples and on urban atmospheres. Meanwhile continued research effort should provide us with new methods which will fill the gaps in our existing arsenal of analytical procedures for aldehydes.

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DONNÉES RELATIVES AUX ÉQUILIBRES CHIMIQUES RÉGISSANT LA SÉPARATION ZIRCONIUM-HAFNIUM

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II. LA TROISIÈME PHASE

Nous avons vu dans la première partie, l'importance du phénomène d'apparition d'une 3ème phase, lorsqu'on extrait des solutions concentrées de zirconium par un faible volume de solvant; on voit alors la phase solvant se partager en deux: (a) une phase riche en tributylphosphate et en zirconium, (b) une phase riche en diluant.

Ce phénomène est gênant dans une installation de production, en ce qu'il oblige à travailler avec des débits de solvants supérieurs à ce qui est nécessaire au simple point de vue du rendement. Nous avons donc été amenés à étudier de près ce problème, à la suite de HUDSWELL *et al.*¹, qui avaient déjà examiné quelques facteurs: rôle du diluant, de la température et de la concentration de la solution aqueuse en acide nitrique et zirconium. Leur travail, très intéressant, était un travail de dégrossissage destiné plutôt à la sélection du diluant. Ces auteurs ont noté en particulier qu'en présence de xylène on n'a jamais trois phases. Un point important, sur lequel HUDSWELL ne donne pas de précisions, est la concentration maximum en zirconium de la phase organique au-delà de laquelle on obtient une démixtion du solvant. Nous avons étudié la variation de cette concentration limite en fonction de divers facteurs qui nous ont semblé devoir jouer un rôle.

Nous examinerons: (1) l'influence de la température, (2) l'influence du % de tributylphosphate dans le solvant, (3) l'influence de l'acidité de la phase aqueuse de départ, (4) l'influence du diluant, (5) l'influence des produits de décomposition du tributylphosphate (cas du dibutylphosphate), (6) l'influence d'une addition d'aromatique (xylène) au diluant.

Nota. Nous savons que l'hexane utilisé comme diluant, se comporte comme la xylène et ne donne jamais de 3ème phase. C'est un solvant dont l'utilisation industrielle paraît intéressante à un autre point de vue: sa faible densité (0.66) et sa faible viscosité (0.32 c.p.) permettent une séparation rapide des phases aqueuse et organique, et par conséquent, des débits plus importants que tout autre diluant, dans une installation industrielle donnée. PHILOON *et al.*² décrivent une installation pour la production d'uranium utilisant l'hexane. Malheureusement, sa grande volatilité et son bas point éclair imposent des précautions irréalisables dans l'état actuel de l'atelier de production français, et nous l'avons pour cette raison, exclu de notre étude.

* Ire Partie: *Anal. Chim. Acta*, 25 (1961) 1.

MODE OPÉRATOIRE

On verse dans une ampoule à décanter successivement 50 ou 60 ml de tributylphosphate, 50 ou 40 ml de diluant, 50 ml d'eau, 50 ml d'acide nitrique concentré (10 ou 12 *N*). Après agitation, décantation et filtration, on obtient environ 100 ml de solvant acide. Nous disposons par ailleurs d'une solution de zirconium dont l'acidité libre (pour la définition de l'acidité, cf. la I^{ère} partie de ce rapport) sera ajustée à 5 ou 6 *N* selon les besoins. À 5 ou 10 ml de solution zirconium, on ajoute, à la burette ou à la pipette, un volume *x* de solvant et on équilibre les phases, par agitation et décantation, dans un thermostat réglé à la température désirée. On ajoute ainsi du solvant jusqu'à ce que la 3^{ème} phase disparaisse. Le zirconium est alors dosé dans la phase solvant.

RÉSULTATS

I. Influence de la température, de la concentration du solvant en tributylphosphate et de l'acidité de la phase aqueuse initiale, sur la concentration limite de zirconium dans une phase solvant homogène

Le diluant est du white spirit "Lavera" soit un mélange de paraffines droites ($d = 0.75$; $130^\circ < E < 190^\circ$).

TABLEAU I

CONCENTRATION EN ZIRCONIUM DANS LA PHASE SOLVANT À LA LIMITE D'APPARITION DE LA 3^{ème} PHASE

Solvant 50-50	6 N	5 N	Solvant 60-40	6 N	5 N
20°	14.5 g/l	14.7 g/l	20°	22.0 g/l	≤ 22.5 g/l
30°	17.8 g/l	17.8 g/l	30°	≤ 26.5 g/l	26.7 g/l

Ces résultats permettent de dégager nettement l'influence des divers facteurs: (1) Importance du coefficient de température*, (2) Influence faible ou nulle de l'acidité de la phase aqueuse (dans les limites expérimentales décrites), (3) Importance de la concentration en tributylphosphate du solvant: en effet, à une diminution de 1/6 de la teneur en tributylphosphate du solvant, correspond une diminution de: $7.4.22 \approx 1/3$ de la teneur limite en zirconium.

II. Influence du diluant

En utilisant la même technique, nous avons essayé de comparer le pouvoir solvant de différents diluants. Les diluants essayés ont été: le white spirit "Lavera", le dodécane, le white spirit fourni par la Société des Hydrocarbures de Saint-Denis, dont on sait seulement qu'il contient moins de 5% d'aromatique. À chacun de ces diluants, nous avons ajouté des proportions croissantes de xylène. Le Tableau II nous donne la teneur limite de la phase solvant à 20° en fonction du % xylène dans le mélange tributylphosphate + diluant + xylène (cf. aussi Fig. 1).

La précision des résultats est de $\pm 3\%$. Ces résultats semblent montrer que le

* Nous avons vérifié que la température dans le domaine considéré était sans influence sur le coefficient de partage du zirconium.

TABLEAU II

Diluant	% xylène	0	5	10				
"Lavera"	Zr g/l φ_s	14.6	20.0	26.8				
Dodécane	% xylène	0	2	5	7	10	15	20
	Zr g/l φ_s	20.7	22.7	25.1	26.7	29.7	35.3	42.5
St. Denis	% xylène	0	2.5	5	10	20		
	Zr g/l φ_s	22.7	23.8	26.5	31	44.7		

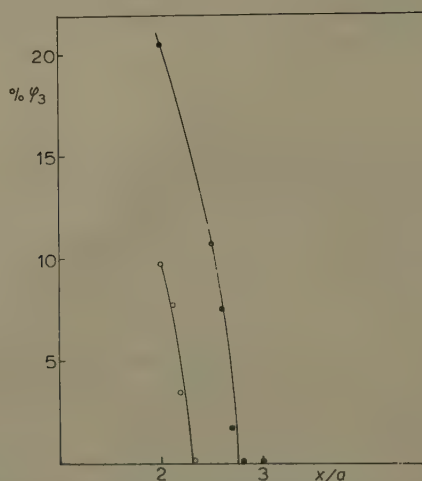


Fig. 1. Importance de la 3^{ème} phase en fonction des rapports de volume solvant/phase aqueuse.
● 2% DBP; ○ 6% DBP.

white spirit des hydrocarbures de Saint-Denis correspond bien — ou équivaut — à un dodécane contenant environ 4% de xylène.

III. Influence des produits de dégradation du tributylphosphate: le dibutylphosphate

Le mode opératoire reste le même: on mélange dans l'ampoule à décanner 50 ml de tributylphosphate, (50 — n) ml de white spirit Saint-Denis, n ml de dibutylphosphate 50 ml d'acide nitrique concentré et 50 ml d'eau; on agite et décante (une logique rigoureuse aurait exigé que le dibutylphosphate fût mis en remplacement du phosphate de tributyle et non du diluant, mais les résultats ne seraient pas exactement comparables aux précédents). Le solvant ainsi préparé sera utilisé, à 20°, suivant la même technique que précédemment: addition à 10 ml de solution aqueuse de zirconium d'une quantité croissante de solvant jusqu'à disparition de la 3^{ème} phase.

Nous avons cette fois noté le volume de la 3^{ème} phase φ_3 , le volume total de solvant, x , et le volume de phase aqueuse, a , et porté sur le tableau les valeurs de φ_3/x en fonction de x/a . Ceci donne une idée de la précision avec laquelle on détermine le point de disparition de la 3^{ème} phase (cf. Tableau III et Fig. 2).

Sachant que pour le solvant initial, sans dibutylphosphate (< 0.1 %), la teneur limite pour le zirconium est 22.8 g/l, on constate que, au moins pour les teneurs qui nous intéressent, la concentration limite en zirconium du solvant augmente pro-

TABLEAU III

	$\frac{x}{a} = \frac{\text{vol } \varphi_s}{\text{vol } \varphi_a}$	2	2.5	2.6	2.7	2.8	3	
2% DBP	φ_3/x	0.20	0.11	0.075	0.017	0	0	$x/a = 2.8 \rightarrow \text{Zr } \varphi_s = 27 \text{ g/l}$
5.92% DBP	x/a	2	2.1	2.2	2.3	2.5		
	% φ_3/x	0.097	0.077	0.034	0	0		$x/a = 2.3 \rightarrow \text{Zr } \varphi_s = 34 \text{ g/l}$

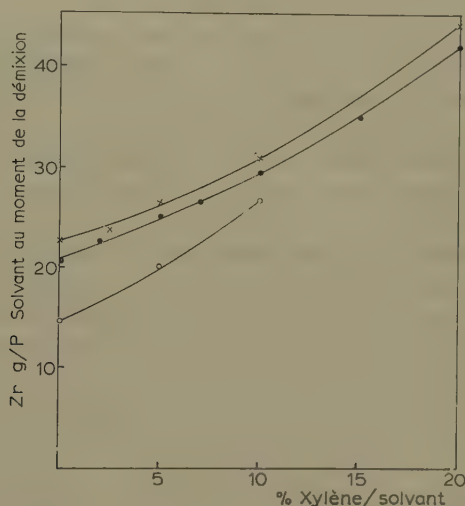


Fig. 2. Teneur limite du solvant en zirconium en fonction de la quantité de xylène présente. Diluants, ○ "white spirit" Lavera; ● dodécane; × "white spirit" St. Denis.

proportionnellement à la teneur en dibutylphosphate et ce, de 2.2 g Zr/l. % de dibutylphosphate. L'influence du dibutylphosphate est donc loin d'être négligeable.

IV. Application pratique: évolution du solvant utilisé pour la production

On constate au fur et à mesure du "vieillissement" du solvant que la concentration limite admissible pour le zirconium augmente au cours du temps. Nous avons pu montrer que ce phénomène était dû à deux causes:

(1) augmentation de la teneur en dibutylphosphate par hydrolyse du solvant, teneur qui est passée de 0.1 à 0.6%.

(2) augmentation de la teneur en tributylphosphate par évaporation du diluant plus volatil: la concentration en tributylphosphate est passée de 50 à 58%. Malheureusement, cette caractéristique n'est pas intéressante pour la production; en effet, l'augmentation de la concentration en dibutylphosphate est génératrice d'émulsions et augmente la rétention du zirconium dans le solvant; l'augmentation de la concentration en tributylphosphate, en augmentant la viscosité du mélange, ralentit la décantation et limite ainsi les débits de liquide admissibles. Une addition

d'aromatiques paraît plus utile si l'on veut accroître la capacité en zirconium du solvant: il devient, en effet, possible d'augmenter la production en gardant un débit total de liquide constant; ce débit total étant évidemment le débit maximum compatible avec un bon fonctionnement des extracteurs.

III. LE VIEILLISSEMENT DU SOLVANT

Nous allons examiner rapidement les effets occasionnés par ce qu'on appelle le "vieillissement" du solvant. Au fur et à mesure des recyclages on constate:

(a) une élévation continue du taux d'extraction du zirconium, que semble accompagner une augmentation de l'extraction du hafnium, d'où production d'une zircone mal déhafniée;

(b) une rétention croissante du zirconium dans le solvant: le lavage à l'eau ne récupère qu'une fraction du zirconium réellement extrait. Cette fraction récupérée est d'autant plus faible que le zirconium a séjourné plus longtemps dans le solvant;

(c) un solvant qu'on a laissé ainsi vieillir, pendant un mois par exemple, en présence de zirconium, devient parfaitement inutilisable même s'il était encore convenable au moment de son stockage: on a, à la fois, des émulsions et des résultats défectueux pour la déhafniation.

On connaît par ailleurs les différents produits de dégradation du tributylphosphate: mono et dibutylphosphate, acide phosphorique et butanol. Enfin, certaines études récentes ont montré³ que, dans le traitement des combustibles irradiés, la présence de très faibles quantités de dibutylphosphate (DBP) était responsable de la mauvaise décontamination de l'uranium, surtout en ⁹⁵Zr.

Notre étude a porté sur la formation du dibutylphosphate au cours du temps et son influence sur l'extraction et la réextraction du zirconium en quantités pondérales.

MODE OPÉRATOIRE

A. Préparation des solutions

Une solution aqueuse de zirconium hafnié contenant 6 moles/l d'acide nitrique libre est notre solution mère. Elle sera ajustée suivant les besoins avec HNO₃ 6 N. Le solvant est un mélange en volume, de 60% de tributylphosphate et 40% d'un diluant: white spirit, xylène ou hexane. Ce solvant est, avant usage, agité avec un égal volume d'acide nitrique 6 N. On extrait avec un volume de solvant acide un égal volume de solution nitrique de zirconium de concentration égale respectivement à 3 et 30 g Zr/l.

Nous avons ainsi préparé 4 solvants chargés en zirconium: (A) tributylphosphate-white spirit contenant 2.7 g/l Zr, (B) tributylphosphate-white spirit contenant 19.7 g/l Zr, (C) tributylphosphate-xylène contenant 19.7 g/l Zr, (D) tributylphosphate-hexane contenant 19.3 g/l Zr.

Chacune de ces solutions représente 1 l de solvant environ. Des aliquotes sont prélevées régulièrement pour suivre la teneur en dibutylphosphate; simultanément on a récupéré par un lavage à l'eau le zirconium qu'elles contenaient.

Lorsque le solvant est frais, la totalité du zirconium (plus de 98%) est récupérée par lavage d'un volume de solvant par un égal volume d'eau; lorsque le solvant a vieilli, l'eau du premier lavage ne contient qu'une partie du zirconium initialement présent dans le solvant. On a vérifié que le zirconium ne passe, dans un second lavage, que dans des proportions très faibles (< 3%).

B. Méthodes analytiques: dosage du dibutylphosphate

Cette méthode est une modification de celle mise au point par la SOCIÉTÉ SAINT-GOBAIN⁴. On utilise le fait que le sel de sodium du dibutylphosphate (DBP Na) est soluble dans l'eau et peu soluble dans les solvants organiques, ce qui permet de le séparer du tributylphosphate.

Par acidification de la phase aqueuse on reforme le dibutylphosphate acide (DBP H) soluble dans les solvants organiques et peu soluble dans l'eau. Une extraction par le benzène sépare donc DBP H des acides minéraux non extractibles; il suffit ensuite de doser par acidimétrie la phase benzénique.

On élimine la majeure partie du zirconium contenu dans le solvant en lavant celui-ci avec H_2SO_4 2 N. Puis on extrait le dibutylphosphate par un mélange de phosphate disodique et de fluorure de sodium (le fluorure en complexant le zirconium restant évite les émulsions possibles par formation de phosphate de zirconium) additionné de Na_2CO_3 pour donner un $\text{pH} \simeq 9$; deux lavages du solvant suffisent (1 volume de solvant + 1/2 volume d'une solution à 20 g/l Na_2HPO_4 + 30 g/l NaF). On acidifie ensuite la phase aqueuse obtenue par HCl concentré et on extrait par deux fois avec 1/2 volume de benzène; la phase benzénique est lavée avec un volume d'HCl 0.1 N puis titrée par NaOH 0.1 N. Au cours de ces différentes extractions qui ne sont pas absolument quantitatives, le dibutylphosphate est récupéré dans la proportion de 96 %, ce qui introduit un facteur correctif dans les calculs.

Si n est le volume en ml de NaOH N/10 versés, et v le volume de la prise d'essai, on a: $\text{DPB } \% = n/v \cdot 2.18$.

Cette méthode permet de doser 20 à 200 mg de dibutylphosphate à ± 5 mg près environ.

RÉSULTATS

Les résultats sont reproduits sur les Tableaux IV, V, VI, VII, et les Figs. 3 et 4. Nous appelons rétention % le rapport:

$$\frac{\text{Zr restant dans le solvant après lavage}}{\text{Zr initialement présent}}$$

TABLEAU IV

SOLUTION B

Diluant: white spirit; Zr/solvant: 19.7 g/l soit 0.216 mole/l; Date: 13.11.1958

Nombre de jours	Zr mg/ml récupéré	Rétention %	‰ DBP	DBP mole/l $\cdot 10^3$	DBP/Zr mole/mole
1	19	3.5	1.0	0.48	0.022
2	18.6	5.5	2.0	0.95	0.044
5	17.4	11.5	5.7	2.72	0.12
7	16.7	15	7.7	3.66	0.17
11		16	8.3	3.96	0.18
15	14.2	28	15.0	7.15	0.33
21	12.7	35.5	19.2	9.15	0.42
29	11.8	40	21.6	10.3	0.47
39	9.6	53			
54	9.0	55	25.7	12.2	0.56
66	7.5	62	46	21.9	1.01

TABLEAU V

SOLUTION A

Diluant: white spirit; Zr/solvant: 2.7 g/l = 0.030 mole/l; Date: 13.11.1958

Nombre de jours	Zr mg/ml récupéré	Rétention %	‰ DBP	DBP mole/l · 10 ³	DBP/Zr mole/mole
3	2.43	11.5	0.5	0.24	0.08
9	2.18	19	1.18	0.56	0.18
11	2.17	20	1.68	0.80	0.26
15	1.97	26	2.30	1.10	0.36
18	1.84	32	2.7	1.28	0.40
25	1.55	42.5	3.2	1.52	0.50
31	1.42	47.5	3.7	1.76	0.58
39	1.32	51.5	4.4	2.70	0.70
64	0.84	69	6.7	3.18	1.06
72	0.70	74			

TABLEAU VI

SOLUTION D

Diluant: hexane; Zr/solvant: 19.3 g/l soit 0.212 mol/l; Date: 3.11.1958

Nombre de jours	Zr mg/ml récupéré	Rétention %	‰ DBP	DBP mole/l · 10 ³	DBP/Zr mole/mole
3	18.3	5	3.5	1.69	0.08
9	16.6	14	9.3	4.43	0.21
12	16.1	16.5	11.7 calc.	5.56	0.27
15			14.2	6.75	0.32
16	15.2	21	15.2 calc.	7.25	0.34
18	14.9	23	17.4	8.30	0.39
25	14	27.5	24.0	11.4	0.54
31	12.4	36	27.0	12.7	0.60
39	12	38	29.0	13.8	0.65
72	8.3	57	59	28.1	1.33

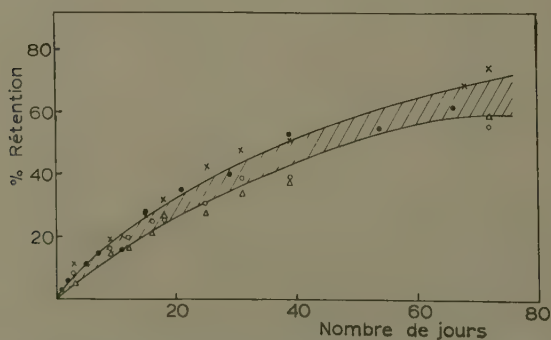


Fig. 3. Rétention du zirconium par le solvant en fonction du temps. ×, Solution A; ● Solution B; Δ Solution C; ○ Solution D.

TABLEAU VII

SOLUTION C

Diluant: xylène; Zr/solvant: 19.7 g/l soit 0.216 mol/l; Date: 3.II.1958

Nombre de jours	Zr mg/ml récupéré	Rétention %	‰ DBP	DBP mole/l · 10 ²	DBP/Zr mole/mole
3	18.1	8	2.86	1.36	0.06
9	16.6	16.8	7.05	3.36	0.15
11			8.2	3.90	0.18
12	15.7	20	9.5 calc.	4.53	0.21
15			12.3	5.86	0.27
16	14.8	25	13.0 calc.	6.20	0.28
18	14.5	26.5	14.0	6.66	0.31
25	13.8	30	18.2	8.76	0.40
31	12.0	39	20.2	9.63	0.44
39	12.0	39	25.5	12.1	0.56
72	8.7	56	42 calc.	19.5	0.90
76			44		

Le ‰ de DBP représente un poids de dibutylphosphate par litre de solvant (tributylphosphate et diluant). Sur la Fig. 3 on voit que la rétention ne dépend pas du diluant. La dispersion des points est raisonnable si l'on tient compte du fait que les diluants ont des volatilités différentes et que les solutions ont pu se concentrer par évaporation au cours des 3 mois de stockage. Les courbes Fig. 4 montrent que la formation du phosphate dibutylique dépend en premier lieu de la quantité de zirconium présente dans le solvant. La quantité de dibutylphosphate formée semble

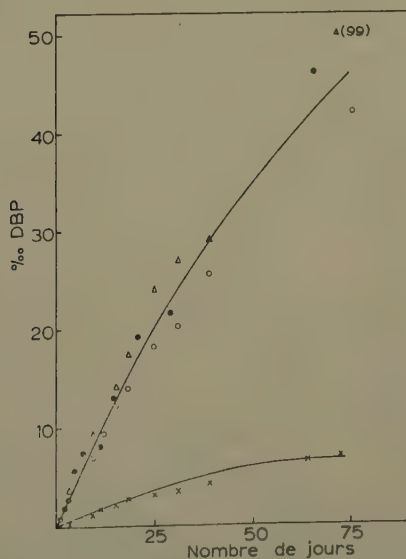


Fig. 4. Formation du DBP en fonction du temps. ○ Solution C; Δ Solution D; ● Solution B; × Solution A.

tendre vers une limite, qui correspond probablement au "bloquage" de la totalité du zirconium présent dans le solvant.

Il existe incontestablement une relation entre la formation du dibutylphosphate et la rétention du solvant. Il nous reste à montrer que le dibutylphosphate est bien seul responsable du phénomène de rétention.

ESSAIS SYNTHÉTIQUES

Ces essais ont été effectués de deux manières différentes:

(a) la première consistait à ajouter du dibutylphosphate à un solvant frais contenant du zirconium et à étudier la réextraction et la rétention;

(b) la seconde consistait à ajouter le dibutylphosphate à un solvant non chargé ce qui permettait d'étudier simultanément l'extraction et la réextraction.

Les deux méthodes ont donné les mêmes résultats, ce qui montre que les équilibres sont rapides. Les Tableaux VIII, IX et X contiennent une partie des chiffres obtenus respectivement avec les diluants: white spirit, hexane. La Fig. 5 traduit la concordance des essais synthétiques et des expériences de vieillissement. Enfin, la Fig. 6 montre bien l'effet du dibutylphosphate sur l'extraction du zirconium.

TABLEAU VIII

ÉTUDE DE LA RÉTENTION DE Zr PAR LE DBP

Diluant, white spirit; Zr dans la solution aqueuse initiale: 30.2 g/l

% DBP	Zr g/l solvant	Extraction %	Rétention %	DBP/Zr mole/mole
0.0	19.5	65	0	0
0.97	19.6	65	1.5	0.021
4.8	20.2	67	8.0	0.10
9.7	20.8	69	13	0.20
19.2	23.1	76	28	0.36
35.0 ^a	19.5		57.5	0.78
49.0 ^a	19.2		74.5	1.12
70.3 ^a	18.7		94	1.63

^a Solutions obtenues par addition de DBP à un solvant contenant 20 g/l Zr

TABLEAU IX

Diluant, white spirit; Zr dans la solution aqueuse initiale: 3.00 g/l

% DBP	Zr g/l solvant	Extraction %	Rétention %	DBP mole/l · 10 ³	DBP/Zr mole/mole
0.45	2.65	86.5	8.5	0.214	0.074
0.9	2.73	89.5	15	0.427	0.14
1.8	2.77	91	22	0.854	0.28
3.6	2.85	93.5	41.5	1.71	0.55
4.5	2.88	94.5	54.5	2.14	0.67
9.0	2.98	97.5	85	4.27	1.29
18	3.05	100	100	8.54	2.58
45	3.05	100	100	17.5	5.47

TABLEAU X

Diluant, hexane; solution, solvant contenant Zr auquel on ajoute du DBP

% DBP	Zr g/l solvant	Zr g/l récupéré	Rétention %	DBP/Zr mole/mole
12.9	19.7	15.3	23	0.28
34.2	19.5	8.2	57.6	0.76
42.4	19.4	6.3	68	0.94
52.8	19.3	4.5	76.7	1.19

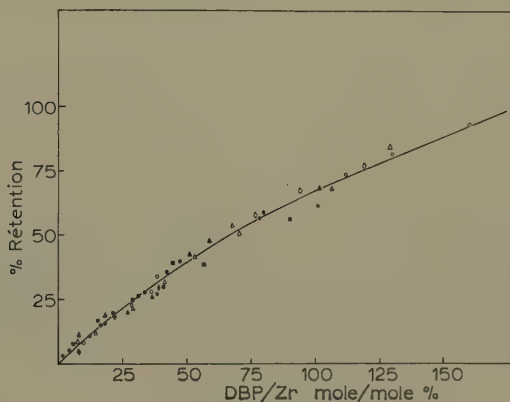


Fig. 5. Rétention en fonction du rapport DBP/Zr molaire.

Diluant	Zr	synthétique	vieillessement
"white spirit"	20 g/l	○	●
"white spirit"	3 g/l	△	▲
xylène	20 g/l	□	■
hexane	20 g/l	◇	◆

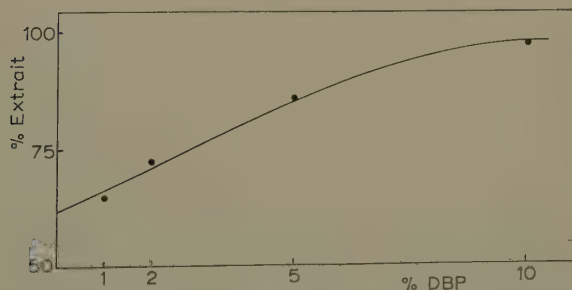


Fig. 6. Influence du dibutylphosphate sur l'extraction du zirconium. Solution aqueuse de zirconium à 20 g/l.

En conclusion, nous pouvons dire qu'il importe de débarrasser le solvant du zirconium qu'il contient, le plus rapidement et le plus complètement possible. À cet égard, une récupération à l'eau, en continu, est préférable à une récupération dis-

continue. L'expérience a montré que cette forme de récupération n'était cependant pas suffisante, et que périodiquement un lavage du solvant par l'acide sulfurique, puis par du carbonate, était nécessaire pour éliminer avec le zirconium, le dibutylphosphate formé.

RÉSUMÉ

La seconde partie de cet article est consacrée plus spécialement au solvant. Les auteurs examinent tout d'abord les conditions de démixtion du mélange de tributylphosphate, de diluant et de zirconium, puis l'interaction du zirconium et du tributylphosphate lorsqu'ils sont abandonnés en présence l'un de l'autre; on montre que le résultat essentiel de cette interaction est la formation du phosphate dibutylque qui possède un fort pouvoir complexant à l'égard du zirconium.

SUMMARY

The chemical equilibria governing the separation of zirconium from hafnium are considered with particular reference to the solvent. The conditions of separation of a mixture of tributylphosphate, diluent and zirconium have been studied as well as the interaction of tributylphosphate and zirconium. The latter results in the formation of dibutylphosphate which has a strong complexing capacity for zirconium.

ZUSAMMENFASSUNG

Es werden die chemischen Gleichgewichte untersucht, von denen die Trennung des Zirkoniums vom Hafnium abhängig ist unter besonderer Berücksichtigung des Einflusses des Lösungsmittels. Die Bedingungen für die Phasenbildung eines Gemisches von Tributylphosphat, Verdünnungsmittel und Zirkonium wurden festgestellt. Es konnte ferner eine Reaktion zwischen Tributylphosphat und Zirkonium nachgewiesen werden, die zur Bildung von Dibutylphosphat führt, das mit Zirkonium einen Komplex bildet.

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ON THE CONCENTRATION AND SEPARATION OF THE TRACE-ELEMENTS Fe, Cu, Zn, Mn, Pb, Mo and Co*

II. SOLVENT EXTRACTION

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INTRODUCTION (CHOICE OF THE SYSTEM)

An extensive literature on the concentration and separation of metals by solvent extraction is available. Reviews have been given by MORRISON AND FREISER¹, BABKO AND ZHAROVSKI² and WEST AND MUKHERJI³. Extractions with organic nitrogen and phosphorus compounds have been reviewed by WHITE⁴. The (discontinuous) extraction technique has the advantage of simplicity and speed.

Concentration is easily accomplished, especially when solvents with a low boiling-point are used.

Separation from macro-constituents is readily achieved. Mutual separations can be obtained in two ways: (1) by the application of several successive extracting agents and/or solvents (WEST³) or (2) with one agent and one solvent only, but using masking-agents and/or different pH values. Of course in both cases, mutual interferences of the extracting or masking agents must be avoided. Thus it is evident that a universal reagent, made selective by changes in the pH, is to be preferred.

Precipitation, under the circumstances required by the extraction process, should be prevented. This is especially important with biological ashes and in general with all samples containing a large excess of inorganic macro-constituents. It forms the main objection against the extraction of the halide and thiocyanate complexes, as these procedures usually require a concentrated solution of the respective anion in which precipitations readily occur.

Combination of extractions with quantitative techniques such as flame photometry, spectrophotometry, neutron activation etc., offers no problem. Combination with spectrophotometry is simple when the extracted complex has a characteristic light absorption, while combination with radiometric techniques is feasible, for example, when a radioactive reagent can be used for the extraction, or when the extracted metal complex can be exchanged with a radioactive metal.

In general however, combination with radiometric techniques (and also with polarography, titrimetry, etc.) poses several problems. Either the reagent used for the extraction should not be extracted or it should easily be evaporated or ashed.

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(The metal complex itself should also easily be ashed). These requirements are a serious objection against the use of aliphatic amines, organic phosphorous compounds, 8-hydroxyquinoline and thenoyltrifluoroacetone.

Only the reagents acetylacetone and diethyldithiocarbamate were considered to fulfill all the requirements mentioned above. Trifluoroacetylacetone could have been used but was not readily available. Xanthate could be used instead of the dithiocarbamate, but it does not allow the extraction of manganese.

Acetylacetone is universal and allows separations to be made by means of pH adjustment. The reagent is coextracted (and in fact is often used itself as a solvent for the metal complexes), but it can easily be evaporated. Metal acetylacetonates can be ashed. The use of acetylacetone as a radioactive reagent is uneconomical as a large excess is required for the extraction*. Radio-exchange of metal acetylacetonates has been studied but without success so far⁵.

Diethyldithiocarbamate is also universal and allows separations to be made by means of pH adjustment. Only a small amount of the reagent is extracted. The metal complexes can easily be ashed. As a rather small excess of reagent is required, the application of the labelled diethyldithiocarbamate is feasible (and in fact has been used for the determination of cobalt⁶). The exchange of the lead from the lead diethyldithiocarbamate with labelled thallium(III) and the exchange of lead with ²⁰⁴Tl-diethyldithiocarbamate have both been applied for the determination of sub-microgram amounts of lead^{5,6}.

ACETYLACETONE

FREISER and his coworkers⁷⁻¹⁴ have been very active in this field. WEST³ used the reagent in combination with other extracting agents (including diethyldithiocarbamate) to achieve a systematical separation of a large group of metals. In general, discontinuous techniques were applied but extractions were never complete in one procedure, even when pure acetylacetone was used. Only molybdate and cobalt(III) were found^{9,12} to be extracted below pH 0.0; iron(III) and copper were extracted at pH 2.0, but for zinc, lead and manganese higher pH values were required; cobalt(II) and iron(II) were not extracted at all.

Experimental

Materials (see also part I)

Acetylacetone (Merck *p.a.*) was neutralised daily by shaking with one volume of 0.01 N sodium hydroxide. All chemicals were again of reagent grade.

Apparatus

Most extractions were carried out with the mixture 1:1 chloroform-acetylacetone in the pyrex glass shaking tubes shown in Fig. 1. Eight tubes were attached with chromium-plated clips to the platform of a home-made aluminium shaker (Fig. 2), the velocity of which could be regulated between 5 and 20 periods per minute. The

* Paper chromatographic separation of ¹⁴C-labelled metal acetylacetonates, which require only a small excess of the reagent, has been studied⁵ without success: traces of the labelled reagent adhered to the paper and gave rise to a variable background.

tubes were filled in position I (the upper meniscus should stand between C and C¹) and emptied in position II. All operations with radio-active solutions were carried out in a shallow trough made of polyethylene.

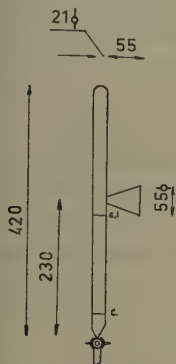


Fig. 1. Pyrex-glass shaking tube for discontinuous extractions.

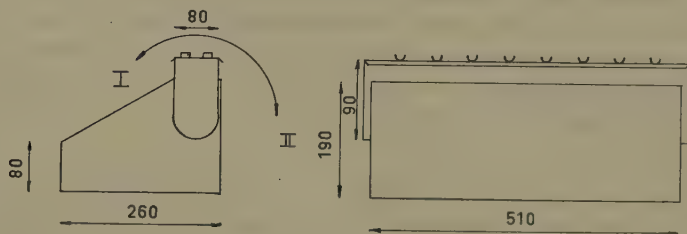


Fig. 2. Aluminium shaker for 8 tubes of Fig. 1.

Pretreatment of the sample

The ashing procedure was described in part I. Residues of perchloric acid had to be removed carefully here, as they interfered with the extraction (see STEINBACH¹²).

Analytical methods

The same methods were applied as in part I. For iron(III), flame photometry^{15,16} or spectrophotometry of the extract can replace the tracer method. The methods of MARONI AND DUBOIS¹⁷ and of CARTLEDGE¹⁸, for the spectrophotometric determination of copper and manganese acetylacetonates respectively, were found to be unsatisfactory. Thus copper was determined as described in part I (after the evaporation and ashing of the extract).

Results

Molybdenum was extracted from 6 *N* sulfuric acid (pH 0.8). As 0.5 ml of concentrated sulfuric acid was used for the ashing, the product had only to be diluted with 2.5 ml of water. With this small aqueous volume a small pill capsule made of PVC with a tightly fitting lid, and of diameter 25 mm and height 76 mm, was more convenient for the extraction. Pure acetylacetone was used instead of a mixture with chloroform, as it was more easily removed from the pill-case. With our procedure (see p. 134) two shakings sufficed for 98% extraction; less than 0.5% of the other trace elements was removed.

A similar result could be obtained for iron and copper at pH 2.0*. As the volume was increased by the neutralisation, either the pill-case (and pure acetylacetone) or the tubes shown in Fig. 1 (and acetylacetone-chloroform) could be used.

All pH values given are starting values. The final pH values were either higher (below pH 5) or lower (above pH 5) than these starting values.

A pH value between 7.5 and 9.5 was required to obtain similar results for manganese and lead. These metals were not extracted below pH 4.0* and 6.0 respectively.

The extraction of zinc and cobalt was incomplete under all circumstances. Only 40% of the zinc was extracted (between pH 6.0 and 9.5) from a solution of the ash of 1 g of dry cow liver. The extraction from a pure zinc chloride solution was only slightly better. For the cobalt, oxidation to cobalt(III) proved to be necessary and was best carried out with hydrogen peroxide at a pH between 8 and 9; the extraction itself was most effective between pH 4 and 5. In contrast to pure cobalt solutions, the cobalt from sample solutions was extracted only very incompletely (about 50%).

Cobalt(III) was unstable below pH 3 and thus extraction below this pH was negligible; but once it had formed, the cobalt acetylacetonate was stable even to acids**.

In conclusion, the acetylacetone extraction of molybdenum, iron, copper, manganese and lead from the solution of a biological ash is feasible, but cobalt and zinc are extracted only to an extent of 50% or less.

DIETHYLDITHIOCARBAMATE

Studies with this reagent have been carried out by many authors and reviews have been published¹⁹⁻²³. Dialkyl, pyrrolidine and other derivatives have also been applied. In general these compounds do not have many advantages, but some are more stable to acids than diethyldithiocarbamate.

Experimental

(see also part I and Experimental p. 130)

All chemicals used were of reagent grade. Mercury solution: 0.1 *M* potassium sodium tartrate containing 160 μg of mercury(II) (as the nitrate) per ml, adjusted to pH 8.5 with sodium hydroxide. The ashing-procedure was as described in part I. Again radio-isotopes were applied to facilitate the evaluation of the results. Copper was determined spectrophotometrically with the reagent itself, following the method of CLULEY²³.

Results

Experiments were again carried out with the ash of 1 g of dry cow liver. The tubes shown in Fig. 1, aqueous and organic volumes of 20 and 10 ml respectively, and a 10-fold excess of diethyldithiocarbamate over the total of the heavy metals were used. To prevent precipitations, 0.2 *M* potassium sodium tartrate was present. With 2 shakings of 5 min each, copper, lead and cobalt were completely extracted at pH values up to 14, zinc only up to 13, and iron and manganese up to 9. Molybdenum was extracted only below pH 5. Separation of copper, lead and cobalt could be obtained by back-extractions with potassium cyanide (Cu), and mercury(II) followed by potassium cyanide (Pb)***.

* This is in contrast to STEINBACH¹², but in accordance with FREISER *et al.*⁹

** This extraordinary behaviour of cobalt was not clearly indicated by either STEINBACH¹² or FREISER *et al.*⁹

*** This technique was used by PŘIBIL *et al.*²⁵ for the spectrophotometric determination of microgram amounts of cobalt and by the present author⁶ for the radiometric determination of sub-microgram amounts of cobalt.

Separation of iron and manganese could not be obtained in a similar way however, although several masking agents were applied (including fluoride, pyrophosphate, nitrate, sulfite, hydroxylamine, cysteine, cysteinamine and "Tiron"). As manganese would have to be determined in the presence of a large excess of iron (with most biological and many other samples), extractions with diethyldithiocarbamate alone were not satisfactory*.

COMBINATION OF ACETYLACETONE AND DIETHYLDITHIOCARBAMATE

Successive extractions with acetylacetone (at pH 2.0) and diethyldithiocarbamate led to a satisfactory procedure. Fortunately the extractions with the diethyldithiocarbamate were only slightly influenced by the presence of the acetylacetone. In Fig. 3 the latter results are shown.

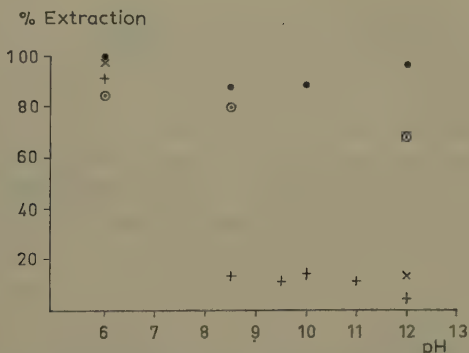


Fig. 3. Extraction of Mn (+), Pb (⊙), Zn (●) and Co (x) from biological ashes, with diethyldithiocarbamate and CHCl_3 (after the extraction of Fe and Cu with acetylacetone). Ammonium ion interferes with the extraction of Zn.

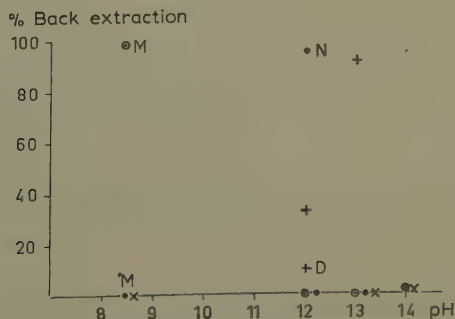


Fig. 4. Back-extraction of Mn (+), Pb (⊙), Zn (●) and Co (x) from the solutions of their diethyldithiocarbamate complexes in CHCl_3 with alkaline tartrate. M: Mercuric solution, N: Ammonia instead of sodium hydroxide. D: in darkness.

Iron could be retained in the aqueous sample solution by adding sodium fluoride up to 0.1 N after the extraction of the zinc. In this way Mn could be separated from Fe. The determination of Fe in the aqueous fluoride solution was complicated appreciably however.

Unfortunately a separation into the groups lead-zinc and cobalt-manganese (by extraction at pH 12 for instance) is not possible: the amounts of the latter metals lost in the lead-zinc fraction are too high. (The behaviour of cobalt is not in accordance with the literature. This may be due to the combined influences of the acetylacetone and the constituents of our sample solutions.)

Thus extraction of all four elements at pH 6.0 was chosen and back-extractions at different pH values were carried out to achieve separation. These back-extractions are shown in Fig. 4.

Obviously the best separation is achieved by successive strippings at pH 13 (Mn), pH 14 (Zn) and pH 8.5 with the addition of mercury(II) (Pb). The mercury diethyldithiocarbamate can be removed with potassium cyanide while the cobalt complex remains in the chloroform.

PROCEDURE

Wet-ash and dilute with water to about 3 ml. Transfer to the pill-case and shake* during 2 min with 3 ml of acetylacetone. Centrifuge for 1 min at 1000 rev./min (ϕ 25 cm) to promote separation and remove the upper layer with a pipet. Repeat this extraction once (the "film" between the two layers is left in the aqueous fraction). Evaporate the acetylacetone and treat the residue with some bromine water (Mo).

Transfer the aqueous layer to the tube of Fig. 1, adjust with ammonia to pH 2.0 (thymol blue) and dilute to 20 ml. Add 10 ml of 1:1 acetylacetone-chloroform and shake for 5 min, with a velocity of 10 periods per minute, in the apparatus of Fig. 2. Remove the extract, repeat the extraction, evaporate the combined organic layers and treat the residue with some bromine water or with a mixture 1:1 nitric acid-hydrogen peroxide (Fe, Cu).

Neutralise the aqueous layer to pH 6 (bromothymol blue), add potassium sodium tartrate to give a 0.1 *M* solution and diethyldithiocarbamate in a tenfold excess over the remaining trace elements.

Shake for 5 min with 5 ml of chloroform, remove the extract and repeat the extraction.

Transfer the combined extracts to a pill-case and strip the chloroform by shaking for 2 min with 5 ml of the following successive solutions: (1) pH 13, (2) pH 14, (3) pH 8.5**, (4) pH 8.5, mercury(II) (see p. 132) and (5) pH 8.5, 1% potassium cyanide, all solutions containing 0.1 *M* potassium sodium tartrate and adjusted to the desired pH with sodium hydroxide.

These solutions then contain: (1) manganese, (2) zinc, (3) no trace elements, (4) lead and (5) mercury. Cobalt remains in the chloroform phase.

CONCLUSIONS

The system chosen, a combination of acetylacetone and diethyldithiocarbamate, has some similarity with the extraction scheme of WEST³. For reasons which were discussed in the introduction, the extractions from acidic chloride and thiocyanate solutions, applied by WEST, had to be omitted. Furthermore our extractions with

* For instance in a "Microid Flask Shaker"

** Solution (3) is required to ascertain the right pH for solution (4); shaking with this solution for only a few seconds is sufficient.

acetylacetone and diethyldithiocarbamate were carried out at higher pH values and several strippings were used by us to separate the diethyldithiocarbamate complexes. By the above method, all metals, except iron and copper are separated. Concentration of the trace elements and separation from the macro-constituents is accomplished. The organic complexes which are introduced can easily be removed.

ACKNOWLEDGEMENTS

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SUMMARY

Extractions with acetylacetone and diethyldithiocarbamate are described. Through the successive application of these reagents the constituents of biological ashes are concentrated and separated into the groups: (1) MoO_4^{2-} , (2) Fe^{+3} , Cu^{+2} , (3) Mn^{+2} , (4) Zn^{+2} , (5) Pb^{+2} , (6) Co^{+3} and (7) Na^+ , K^+ , Ca^{+2} , Mg^{+2} , SO_4^{2-} , PO_4^{3-} .

RÉSUMÉ

Des extractions au moyen d'acétylacétone et diéthylthiocarbamate sont décrites, en vue d'une séparation des divers constituants des cendres biologiques (Fe, Cu, Zn, Pb, Mo, Co).

ZUSAMMENFASSUNG

Es werden Extraktionen mit Acetylacetone und Diaethylthiokarbamat beschrieben. Durch geeignete Anwendung dieser Reagenzien können die Bestandteile von biologischen Aschen in folgende Gruppen getrennt werden: (1) MoO_4^{2-} , (2) Fe^{+3} , Cu^{+2} , (3) Mn^{+2} , (4) Zn^{+2} , (5) Pb^{+2} , (6) Co^{+3} und (7) Na^+ , K^+ , Ca^{+2} , Mg^{+2} , SO_4^{2-} , PO_4^{3-} .

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INDIRECT OXIDIMETRIC DETERMINATION OF CERTAIN α -AMINO ACIDS WITH VANADIUM(V)

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α -Amino acids which are smoothly oxidised quantitatively by certain 1,2-glycol splitting reagents such as periodic acid¹ and lead tetraacetate² are resistant to certain other oxidants such as cerium(IV)³ and vanadium(V). The de-aminated products of the amino acids with nitrous acid, *i.e.* the α -hydroxy acids, can however be oxidised easily by these oxidants. TAKAHASHI *et al.*³ have developed an indirect method for the determination of α -amino acids via oxidation of the de-amination products but the results are not strictly stoichiometric and empirical factors calculated from pure compounds are required. Studies on the oxidation of organic compounds by vanadate solution in these laboratories have shown that vanadate is a milder and more specific oxidant for organic compounds than cerium(IV). The present communication describes a study of the oxidation of the de-amination products of the α -amino acids with a view to developing a method for their determination; the reactions are more stoichiometric than with cerium(IV).

It has also been shown that pure vanadium pentoxide can be used as a primary standard.

EXPERIMENTAL

Preparation and standardisation of vanadate solution from vanadium pentoxide

Earlier workers^{4,5} have recommended either ammonium vanadate or sodium metavanadate for the preparation of vanadate solutions. BISHOP AND CRAWFORD⁵ have shown that pure ammonium vanadate can be used as a primary standard but it is generally preferred to standardise the solution before use. RAO *et al.*⁴ converted ammonium vanadate to the sodium salt by boiling with slight excess of sodium carbonate till the smell of ammonia ceased and decomposed excess carbonate with acid but this method is laborious. Therefore it was thought better to use vanadium pentoxide for preparing sodium vanadate solution.

The vanadium pentoxide used in the present investigation was an A.R. sample supplied by Baker which was stated to have 100% assay. Analytically pure vanadium pentoxide can also be prepared by decomposing twice crystallized ammonium metavanadate in a platinum crucible in presence of air at a temperature of 400°–500° and storing the material in a desiccator. Vanadium pentoxide which consists of cinnabar red rhombic crystals, is only slightly soluble in water giving an acidic reaction, but dissolves freely in alkaline solution to form colourless vanadate solution. On acidification the solution turns yellow but does not reprecipitate at low concen-

rations (*cf.* As_2O_3). Solutions of exact strength can be prepared by this method and are free from ammonium ions. According to JANDER AND JAHR⁶, polyvanadates exist as an equilibrium mixture in the solution depending on its pH. But this does not affect the usual oxidising properties of the vanadate solution.

The vanadate solution was prepared by shaking a weighed quantity of vanadium pentoxide in approximately 1.0 *N* sodium hydroxide until dissolution was complete. The solution was then diluted to the mark in a volumetric flask. The strengths of the solutions were checked by titrating against a standard ferrous ammonium sulphate solution, the strength of which was determined by potassium dichromate solution, *N*-phenylanthranilic acid being used as internal indicator. The results of the standardisation given in Table I indicate that the vanadium pentoxide can be used satisfactorily as a primary standard.

TABLE I

<i>Vanadium pentoxide taken (g)</i>	<i>Vanadium pentoxide found (g)</i>
9.0856	9.0910
8.8792	8.8600
10.1224	10.1340

Amino acid solutions

Fresh 0.02 *M* solutions of pure amino acids (DL-alanine, DL-norleucine, and D-glutamic acid) were prepared by dissolving the requisite amount of pure amino acids in distilled water.

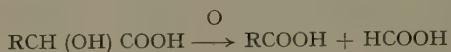
General procedure for de-amination and oxidation of amino acids

To an aliquot of the amino acid solution in a 250-ml conical flask fitted with reflux condenser, approximately 1 ml of 30% sodium nitrite solution and 10 ml of 3 *N* sulphuric acid together with 20 ml of distilled water were added and the solution was boiled till a drop of the solution gave no colour with starch-iodide paper. A known excess of 0.1 *N* vanadate solution was added and the overall acid concentration was adjusted to approximately 12 *N*. The solution was refluxed on a water bath for 30 min and then cooled. The excess of vanadate in the solution was determined by back-titration with standard ferrous ammonium sulphate solution potentiometrically or with *N*-phenylanthranilic acid as indicator. From the amount of vanadate consumed the equivalents of oxygen consumed per mole of the amino acid was determined. The results are given in Table II.

TABLE II

<i>Amino acid</i>	<i>Amount of 0.02 M amino acid (ml)</i>	<i>Amount of 0.1 N vanadate solution (ml)</i>	<i>Equivalents of oxygen consumed per mole of amino acid</i>	
			<i>found</i>	<i>calculated</i>
DL-Alanine	5.0	5	2.15	2
DL-Norleucine	4.0	5	2.03	2
D-Glutamic acid	3.5	5	4.32	4

From Table II it is evident that the equivalents of oxygen consumed correspond to the oxidation to formic acid and higher fatty acids according to the general equations:



and that the reactions are more or less stoichiometric.

DISCUSSION

It has been shown that the oxidation of the de-amination products of the α -amino acids with vanadate provides a more satisfactory method for their determination than oxidation by cerium(IV) and the use of empirical corrections can be eliminated. The success of the method depends to a very great extent on complete elimination of nitrous acid, on preventing the loss of the decomposition products of α -hydroxy acids, and on preventing further oxidation of formic acid. That formic acid is not oxidised to a measurable extent under these conditions is well established and the loss of volatile decomposition products, *i.e.* the aldehydes and the formic acid, can be minimised by circulating cold water through the reflux condenser. The method can also be applied for the determination of a mixture of two or more amino acids.

ACKNOWLEDGEMENT

The authors express their thanks to Prof. K. P. HALDAR, Head of the Department of Chemistry, for his keen interest in the work.

SUMMARY

A method for preparing standard vanadate solution using pure vanadium pentoxide as primary standard is described. The determination of certain α -amino acids by oxidation of their de-amination products with standard vanadate solution is studied.

RÉSUMÉ

Une méthode est proposée pour le dosage de certains acides α -aminés; on traite la solution à analyser par une solution de vanadium(V), dont on titre l'excès par le fer(II).

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung gewisser α -Aminosäuren durch Behandlung mit einer Vanadium-(V)-Lösung, deren Ueberschuss mit einer Eisen-(II)-Lösung zurücktitriert wird.

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QUANTITATIVE ASPECTS OF THE OXIDATION OF ALIPHATIC ALCOHOLS BY POTASSIUM PERMANGANATE

I. METHANOL AND ETHANOL

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Further investigation of the use of redox titrations for the determination of simple aliphatic alcohols was prompted by the unsatisfactory features of the available volumetric methods. Several workers¹⁻⁴ have reported the use of dichromate for the determination of methanol, ethanol and 2-propanol; the present paper deals with quantitative aspects of the oxidation of methanol and ethanol by acidified permanganate solutions. Earlier workers have examined the use of acidified and alkaline solutions of permanganate for such determinations⁴, but none of these methods appears to be very satisfactory and the effect of catalysts does not seem to have been studied. In the present work, conditions for the quantitative conversion of methanol to carbon dioxide have been established for fairly low concentrations of this alcohol, but no simple stoichiometric relationship could be found for the oxidation of ethanol under similar conditions.

EXPERIMENTAL

All reagents used were of analytical reagent grade. Solutions of sodium thiosulphate,

TABLE I
COMPOSITION OF REACTION MIXTURES INVESTIGATED
All molarities refer to reaction mixture

Molarity of alcohol		Moles/mole of alcohol		Molarity of catalyst		Reaction temperature (°C)	Optimum reaction time (h)
MeOH	EtOH	KMnO ₄	H ₂ SO ₄	Mn ²⁺	Ammonium molybdate		
0.003	—	0.60	100.0	0.0015	—	45	24
0.01	—	2.84	94.8	0.0200	—	45	12
0.01	—	2.84	96.7	—	0.0398	50	4
0.01	—	2.69	102.5	—	0.0398	60	1½
0.01	—	5.82	92.0	—	0.0398	60	1
0.005	—	2.94	208.2	—	0.0796	60	2½
0.005	—	5.87	182.7	—	0.0796	60	2
0.0025	—	5.68	413.8	—	0.1582	60	3
0.0025	—	9.35	370.2	—	0.1582	60	2
—	0.01	2.70	91.4	—	0.0398	18	3

iodine, sulphuric acid and potassium permanganate were standardised against potassium iodate by conventional methods.

Oxidation procedure

Solutions of the reactants and catalyst were mixed in a 250-ml flask, fitted with a ground-glass stopper, which was immersed in a thermostat at the required temperature. Typical reaction conditions with optimum reaction times are shown in Table I.

Determination of permanganate consumed

After the reaction, excess of permanganate was determined iodometrically, the mixture being diluted with an equal volume of water and cooled rapidly to room temperature before addition of potassium iodide solution. Appreciable thermal decomposition of permanganate occurred during the reaction period, especially at the higher temperatures used; an appropriate correction was, however, determined in blank experiments and applied.

Determination of carbon dioxide

In certain cases (Tables II and III) the carbon dioxide produced during the oxidation was measured directly. Carbon dioxide-free air was drawn slowly through the

TABLE II

EXTENT OF CONVERSION OF METHANOL TO CARBON DIOXIDE FROM PERMANGANATE CONSUMPTION AND FROM EVOLVED CARBON DIOXIDE

Temperature: 60°

Reaction mixture		Uptake of KMnO_4 (moles/mole MeOH)		% Methanol completely oxidised from	
Molarity of MeOH	Moles KMnO_4 per mole MeOH	Mean value (10 determinations)	Maximum deviations	KMnO_4 uptake	Direct determination of evolved CO_2
0.0025	9.35	1.23	± 0.02	102.5	102.8
0.005	5.87	1.21	± 0.01	100.8	99.6
0.010	2.69	1.12	$\left\{ \begin{array}{l} + 0.01 \\ - 0.02 \end{array} \right.$	93.3	93.4

TABLE III

EXTENT OF CONVERSION OF ETHANOL TO ACETIC ACID AND CARBON DIOXIDE

Temperature: 18°

KMnO_4 uptake for		Wt. of evolved CO_2 (mole/mole EtOH)	KMnO_4 uptake	
Complete reaction	Reactions other than stages a and b		Needed to form evolved CO_2	Due to "induced decomposition"
0.965	0.165	0.029	0.023	0.142

* Initially in reaction mixture: $[\text{EtOH}] = 0.01 \text{ M}$; $[\text{MnO}_4^-] : [\text{EtOH}] = 2.70$. Moles EtOH present = $5.02 \cdot 10^{-4}$

** All KMnO_4 uptake values are in moles KMnO_4 /mole EtOH in reaction mixture. Reaction stages a and b refer to the oxidation sequence given for ethanol (see Discussion).

reaction mixture and then through a series of wash-bottles containing barium hydroxide solution. With 0.01 M alcohol concentrations, barium carbonate was precipitated from a saturated barium hydroxide solution, filtered off, dried and weighed. With more dilute alcohol solutions, excess of 0.05 N barium hydroxide solution was titrated with 0.05 N hydrochloric acid, with phenolphthalein indicator; carbon dioxide-free nitrogen was passed over the hydroxide solution and the acid was added slowly, with vigorous shaking, to minimise reaction with the barium carbonate.

Determination of carbon monoxide

Carbon dioxide-free air was bubbled through the reaction mixture, as above, and then passed through two U-tubes containing "Sofnolite", to absorb any carbon dioxide, and magnesium perchlorate. Hopcalite (activated manganese dioxide) at 120° was then used to convert carbon monoxide to carbon dioxide, which was absorbed in saturated barium hydroxide solution and determined gravimetrically as barium carbonate.

Detection of formaldehyde

Samples of reaction mixtures containing methanol and acidified permanganate were withdrawn at intervals. The permanganate colour was discharged with sulphur dioxide, and SCHRYVER's test⁵ for formaldehyde was applied. Blank tests showed that sulphur dioxide did not interfere with the test.

RESULTS AND DISCUSSION

Choice of catalyst

Exploratory work showed that a 0.01 M solution of methanol is not appreciably oxidised by acidified permanganate after 24 h at room temperature, but that the reaction is catalysed by manganese(II). Oxidation is extensive with this catalyst at 45°, but variable results (reproducibility $\pm 3\%$) were obtained, possibly due to the competitive reaction between permanganate and manganese(II)⁶, and an alternative catalyst was therefore sought. Molybdate and vanadate ions were tested and quanti-

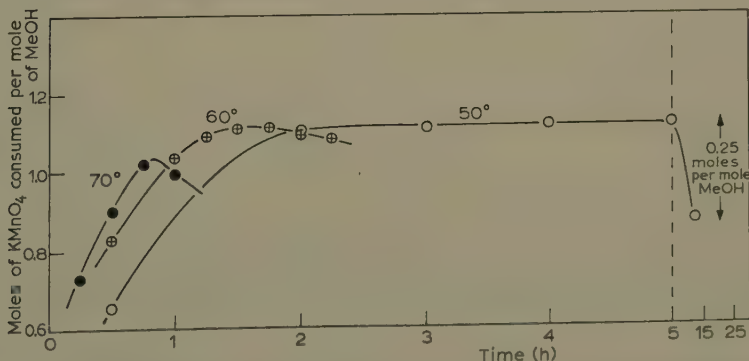


Fig. 1. The influence of temperature on rate of permanganate consumption by methanol. $[\text{MeOH}]$ initially present = $5 \cdot 10^{-4}$; $[\text{KMnO}_4]$: ○ = 0.0284 M , ⊕ and ● = 0.0269 M .

tative investigations showed that ammonium molybdate was superior to manganese(II). Thus, oxidation of 0.01 *M* solutions of methanol at 60°, and of ethanol at room temperature, gave titration values which were reproducible to $\pm 0.5\%$.

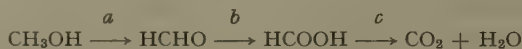
Choice of reaction temperature

Variation with temperature of the time required for maximum uptake of permanganate by an 0.01 *M* solution of methanol is shown in Fig. 1. A temperature of 60° was chosen for the oxidation of less than 0.01 *M* methanol solutions because the maximum uptake of permanganate was then obtained after only 1–2 h.

In 0.01 *M* solution, ethanol was oxidised more rapidly than methanol and the optimum reaction time at room temperature was only 3 h (Table I). This result agrees with observations on the relative rates of 'induced oxidation' of aliphatic alcohols by acidified permanganate⁷.

Stoichiometry

(a) *Methanol*. Total oxidation of methanol by permanganate probably proceeds by the series of reactions:



each stage involving one atom of oxygen. The existence of stage *a* was indicated by a positive test for formaldehyde, during the first 15 min of the oxidation of a 0.01 *M* solution of methanol.

The amounts of permanganate needed to oxidise methanol in various concentrations were determined by allowing the reaction to proceed at 60° in the presence of the catalyst, until the residual oxidising power remained constant. The excess of oxidising agent was varied for each of the methanol concentrations studied (see Fig. 2).

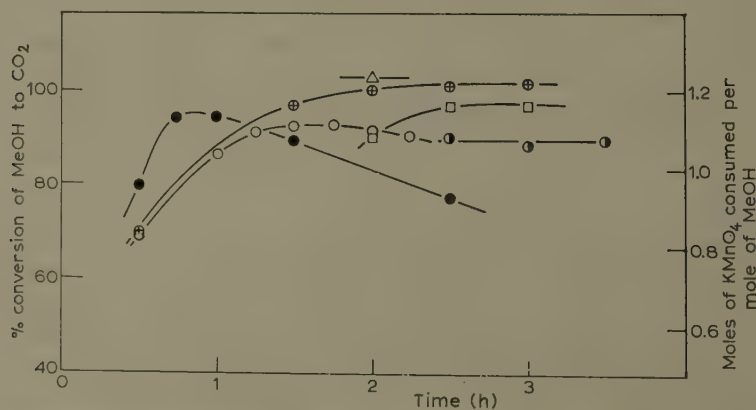


Fig. 2. Influence of concentrations of methanol and permanganate on extent of conversion of methanol to carbon dioxide. Temperature = 60°. $[\text{MeOH}]$ $[\text{MnO}_4^-] : [\text{MeOH}]$

0.01 <i>M</i>	$\left\{ \begin{array}{l} 2.69 \circ \\ 5.82 \bullet \end{array} \right.$
0.005 <i>M</i>	$\left\{ \begin{array}{l} 2.94 \circ \\ 5.87 \oplus \end{array} \right.$
0.0025 <i>M</i>	$\left\{ \begin{array}{l} 5.68 \square \\ 9.35 \triangle \end{array} \right.$

After reaching a maximum value, the consumption of permanganate decreased with time, apparently because of an increased rate of thermal decomposition of permanganate. The decomposition with time of 0.0284 M permanganate in blank experiments at 50° is shown in Fig. 3.

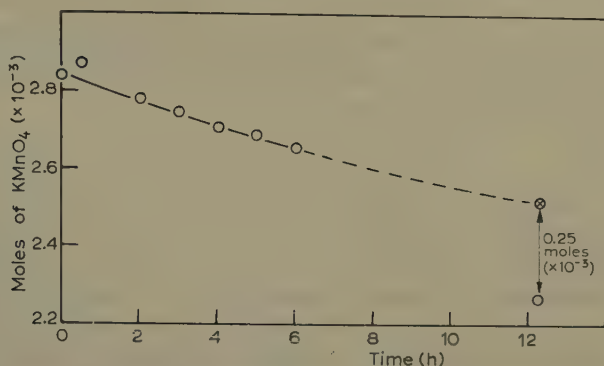


Fig. 3. Decrease in concentration of permanganate in "blank" experiments (cf. Fig. 1 and Table I). Temperature = 50° ; $[\text{MnO}_4^-] = 0.0284\text{ M}$; $[\text{H}_2\text{SO}_4] = 0.967\text{ M}$; $[\text{Molybdate ion}] = 0.0398\text{ M}$.

The oxidising power of the 'blank' solution after about 12 h was $0.25\text{ mole} (\times 10^{-3})$ of permanganate less than the extrapolated value, a decrease closely comparable with the decline in permanganate uptake observed in the reaction solution (Fig. 1). This decomposition of permanganate may well occur on the surface of precipitated manganese dioxide⁸⁻¹⁰.

It can be seen from Fig. 2 that, when 0.005 M and 0.0025 M solutions of methanol were treated with a six- and nine-fold excess of permanganate respectively, the uptake of permanganate agreed well with the theoretical requirement ($1.2\text{ mole KMnO}_4/\text{mole MeOH}$). Direct determination of the evolved carbon dioxide confirmed that quantitative conversion of methanol to carbon dioxide had been achieved (Table II).

When a 0.01 M solution of methanol was treated with a three-fold excess of oxidant, the uptake of permanganate was $1.12\text{ mole KMnO}_4/\text{mole MeOH}$, which corresponded to conversion of 93.3% of the alcohol to carbon dioxide and was confirmed by direct gravimetric determination of the carbon dioxide evolved (Table II). Gravimetric determination of carbon monoxide in the evolved gases showed that only traces were formed (equivalent to $< 0.5\%$ of the total carbon dioxide evolved). The extent of oxidation of methanol was only slightly increased by increasing the excess of oxidant; e.g. with a six-fold excess the uptake was only $1.13\text{ mole KMnO}_4/\text{mole MeOH}$ corresponding to 94.2% conversion to carbon dioxide.

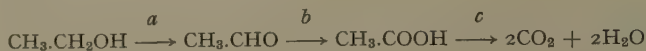
The above experiments show that the extent of oxidation of methanol to carbon dioxide is increased by dilution of the methanol, and by the use of a larger excess of oxidant. In terms of the proposed reaction path, the results obtained suggest that, whilst stage *a* is fast and either stage *b* or *c* is rate determining, stage *b* competes with a process *d*: $n\text{HCHO} \rightarrow (\text{HCHO})_n$, which leads to the formation of an acid-stable polymer¹¹. Thus:

$$\begin{aligned} \text{Total rate of HCHO consumption} &= \text{Rate of oxidation via stage } b + \text{Rate of polymerisation via stage } d \\ &= k_1 \cdot [\text{HCHO}]^x \cdot [\text{MnO}_4^-]^y + k_2 \cdot [\text{HCHO}]^z \end{aligned}$$

It can be seen that successful competition of process *b* with process *d* would be favoured by decreasing the concentration of methanol (and hence of formaldehyde formed via stage (*a*)) and increasing that of permanganate.

(*b*) *Ethanol*. The oxidation of a 0.01 *M* solution of ethanol by a three-fold excess of permanganate, in the presence of ammonium molybdate catalyst, was investigated at room temperature. When the oxidising power of the residual solution reached a constant value, 0.965 mole KMnO_4 /mole EtOH were found to have been consumed.

The probable course of the oxidation is:



in which each of the stages *a* and *b* require one atom of oxygen, whilst stage *c* requires 4 atoms of oxygen. Thus, the observed permanganate consumption suggests that, in addition to the complete oxidation of ethanol to acetic acid, requiring 0.8 mole KMnO_4 /mole EtOH , partial oxidation of acetic acid to carbon dioxide had occurred, requiring a further 0.165 mole KMnO_4 /mole EtOH (Table III). Gravimetric determination (as barium carbonate) of the carbon dioxide evolved showed that conversion of acetic acid to carbon dioxide accounted for only 0.023 mole KMnO_4 /mole EtOH (Table III), thus leaving an unaccounted uptake of 0.142 mole. Since more extensive precipitation of manganese dioxide was observed in the reaction mixture than in blank experiments, the discrepancy may be due to an 'induced decomposition' of permanganate promoted by the ethanol.

CONCLUSIONS

Manganese(II) and molybdate ions effectively catalyse the oxidation of simple alcohols by acidified potassium permanganate solution, the molybdate being superior in giving more reliable results. With molybdate catalyst and under the conditions described, the reaction may conveniently be used to determine methanol in solutions of fairly low concentration. The reproducibility for the concentrations studied is within $\pm 3\%$. For more concentrated methanol solutions and for ethanol solutions the reaction is non-stoichiometric, apparently due to competing side-reactions.

ACKNOWLEDGEMENTS

The author wishes to acknowledge his gratitude to Dr. C. F. CULLIS of Imperial College for his unfailing interest and much valuable discussion, to W. G. NORTHCROFT for assistance with experiments involving formaldehyde and to Shell International Petroleum Company Limited and The Royal Society for grants in respect of materials and apparatus.

SUMMARY

The quantitative oxidation of methanol and ethanol by acidified potassium permanganate solution has been studied. Molybdate is superior to manganese(II) as the catalyst. In fairly dilute methanol solutions a large excess of permanganate oxidises the alcohol quantitatively to carbon dioxide. With ethanol, oxidation proceeds beyond the acetic acid stage but the further reaction is not stoichiometric.

RÉSUMÉ

Une étude a été effectuée sur l'oxydation des alcools méthylique et éthylique par le permanganate de potassium en milieu acide. Comme catalyseur, le molybdate s'est montré supérieur au manganèse (II).

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die quantitative Oxydation von Methanol und Äthanol mit saurer Kaliumpermanganatlösung. Als Katalysator erwies sich Molybdat dem Mangan-(II) überlegen. Bei Äthanol verläuft die Oxydation nicht stöchiometrisch.

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1,8-DIHYDROXYANTHRAQUINONE AS A REAGENT FOR BORIC ACID AND ITS USE IN THE ANALYSIS OF PHARMACEUTICAL GRADE GLASS

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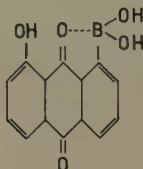
The need to evaluate traces of boric acid, amounting to only a few μg , arising from hydrolytic transfer from pharmaceutical glasses, has led to a search for a highly sensitive procedure which would be simple to apply for quantitative work.

The best known methods in the literature are those which depend on the enhancement of the acidity of boric acid by polyhydroxy compounds, *viz.* glycerine^{1,2}, mannitol^{3,4}, pentamethylenequercitol⁵, levulose, invert sugar or propylene glycol⁶. Such reactions may be made more sensitive by the use of potentiometric methods⁷, high frequency methods^{8,9}, polarographic methods¹⁰, polarimetric methods with tartaric acid¹¹ or complexometric methods¹². The reaction between boric acid and fluoride in which hydroxyl ions are released, has been utilized colorimetrically¹³. The reaction between iodide and iodate with starch in presence of boric acid can only be used qualitatively¹⁴. In any case, all these methods require extractions, prior decompositions or titrations of very dilute solutions and so are unsuitable for rapid routine work.

1,8-Dihydroxyanthraquinone was investigated therefore as a reagent for boric acid.

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It belongs to the hydroxyanthraquinone group and forms with boric acid in the presence of sulfuric acid a peri-hydroxy compound with heterovalent inner bonds¹⁵; the sulfuric acid acts as a dehydrating agent. The actual composition of the complex formed is:



Various anthraquinone derivatives have already been described for the detection of boric acid¹⁶. For example, purpurin (1,2,4-trihydroxyanthraquinone) shows an identification limit of 1 μg of boron, alizarin S (1,2-dihydroxyanthraquinone sulfonic acid) shows a limit of 0.60 μg of boron, and quinalizarin (1,2,5,8-tetrahydroxyanthraquinone) 0.06 μg of boron. All these reagents are eminently suitable for the detection of boric acid in glass containers intended for pharmaceutical use, and quinalizarin is particularly sensitive, but none of the reagents mentioned yields a color intensity which is proportional to the boric acid concentration.

On the other hand, 1,8-dihydroxyanthraquinone, which is widely used as a cathartic under various trade names such as Istizin, Chrysazin, etc., and is readily available in a pure form, is almost as sensitive as quinalizarin and turns distinctly from brilliant red to purple red on addition of boric acid. Since the color formed is not pure, but rather a superposition of two colors, Beer's law is not obeyed at the maximum absorbancies at 340 and 580 $\text{m}\mu$, but satisfactory results can be obtained at the latter wavelength if a calibration curve is used. Moreover, 1,8-dihydroxyanthraquinone forms a bright pink fluorescent complex with boric acid which can be utilized quantitatively although the sensitivity is lower than the spectrophotometric reaction.

The method proposed is extremely simple and can be used in the cold; heating increases both the absorbance and the fluorescence slightly, but the relationship between the boric acid concentration and the measurement is then less regular. The color is reasonably stable and readings can be made between the 30th and 60th min, or within 2 h if a slight decrease in color intensity is allowed for.

The reaction has been examined for the detection and determination of boric acid from pharmaceutical grade glass ampoules, the qualitative tests being carried out on whole ampoules and the quantitative tests on powdered glass. When the sensitivity of the 1,8-dihydroxyanthraquinone reaction is compared with that of the above-mentioned reagents of the anthraquinone group, it is possible to establish the limits of boric acid for a good grade glass.

EXPERIMENTAL

Apparatus

Spectrophotometer C.G.A. model 200/23. Fluorimeter C.G.A. C/S model 2/3.

Reagents

1,8-Dihydroxyanthraquinone, 0.2% in concentrated sulfuric acid. 1,2,4-Trihydroxyanthraquinone, 0.5% in concentrated sulfuric acid. 1,2-Dihydroxyanthraqui-

none-3-sulfonic acid, 0.2% in concentrated sulfuric acid. 1,2,5,8-Tetrahydroxyanthraquinone, 0.01% in concentrated sulfuric acid.

Procedures

Spectrophotometric determination. Solutions containing 0.1, 0.2, 0.3..... μg of boric acid per ml were prepared in concentrated sulfuric acid containing 0.2 % 1,8-dihydroxyanthraquinone reagent. The absorbancies were read at 580 $m\mu$ against the blank reagent between 30 min and 1 h after mixing. The calibration curve was prepared in this way (Fig. 1).

Fluorimetric determination. Solutions were prepared in the same way as for the spectrophotometric method but the amounts of boric acid taken were 0.5, 1.0, 1.5..... $\mu\text{g}/\text{ml}$. The readings were taken using a blue filter 20–40 min after mixing.

Application for the method to the detection and determination of boric acid in pharmaceutical grade glass

Qualitative test. Dilute one drop of the several anthraquinone reagents under consideration with 0.5 ml of concentrated sulfuric acid for ampoules up to 3 ml and

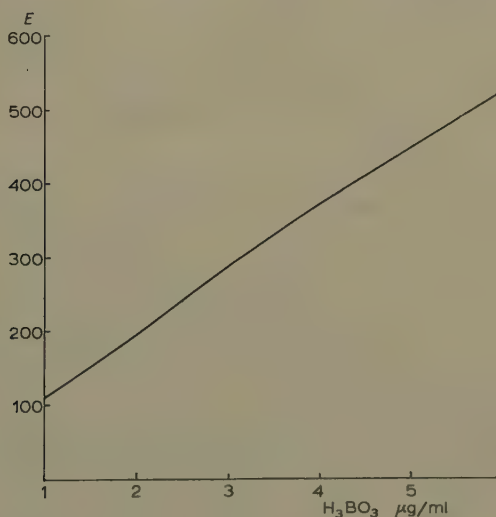


Fig. 1.

TABLE I
BEHAVIOUR OF A GOOD PHARMACEUTICAL GRADE GLASS WITH ANTHRAQUINONE REAGENTS

Reagent	Time for color change	Tone of color
1,2,4-Trihydroxyanthraquinone (Purpurin)	None within 24 h	From red to cherry red (not clean)
1,2-Dihydroxyanthraquinone-3-sulphonic acid (Alizarins)	Slight within 30 min	From yellow to red (clean)
1,8-Dihydroxyanthraquinone (Istizin, Crisizin)	Slight within 5 min	From red to purple red (clean)
1,2,5,8-Tetrahydroxyanthraquinone (Quinalizarin)	50% of the ampoules change color within 5 min	From purple to light or sky blue (clean)

with 1 ml of concentrated sulfuric acid for larger ampoules or containers. Heat gently over a moving flame. The color changes obtained are described in Table I.

Thus, if the times for the various color changes are compared, a limit for the boric acid surface losses or transfers for a pharmaceutical grade glass can be established.

Quinalizarin and Istizin are sufficient for this purpose; in addition to reducing the observation times, this allows the detection of boric acid and the determination of a maximum limit.

It is possible to state therefore that an acceptable pharmaceutical grade glass must satisfy the last two tests shown in Table I.

Determination of boric acid in a pharmaceutical grade glass. Crush the glass in a bronze mortar and remove any metallic particles by passing a magnet several times over it. Collect the glass powder which passes through a No. 35 sieve but is retained on a No. 55 sieve. Wash by decantation with 15-, 10- and 10-ml portions of water and with two 10-ml portions of ethanol, draining well each time. Dry at 120° for 30 min.

The glass particles thus obtained allow easy decantation: a smaller size, *i.e.* 80/100, yields sulfuric acid extracts which must be cleared by centrifugation and which increase the extraction by a mere 10–15%.

Weigh 15 g of the glass powder so prepared and transfer it to a 50-ml frosted heat-resistant glass flask, add concentrated sulfuric acid to 4/5 of the volume and leave for 12 h at room temp., shaking gently at frequent intervals. Fill at the same time a glass flask (without powdered glass) with concentrated sulfuric acid nearly to the mark, keeping it for use as blank.

After 12 h, add 1 ml of 1,8-dihydroxyanthraquinone reagent and bring to the required volume with concentrated sulfuric acid. Treat the flasks containing the powdered glass under test, the standard and the blank in the same way. Take readings against the reagent blank at 580 m μ , as mentioned elsewhere. Use old glassware, whose boric acid surface transfers are absolutely negligible and do not therefore interfere with an accurate determination. For the calculation bear in mind that the 15 g of powdered glass is usually equivalent to 7.5 ml; the sulfuric acid extract inside a 50-ml glass flask corresponds to 42.5 ml.

Iron(III), nickel(II), cobalt(II) and chromium(III) do not interfere up to a quantity corresponding to half of the boric acid, and only slightly when they reach an equal amount. Therefore, an evaluation of boric acid contents in colored pharmaceutical grade glass is possible.

We have tested about 30 pharmaceutical grade glasses of different production, both

TABLE II

Weighed No. 35–55 glass powder	Sample No.	H ₃ BO ₃ transfer μ g
g 15	1	61
g 15	2	66
g 15	3	56
g 15	4	157
g 15	5	103
g 15	6	122
g 15	7	38
g 15	8	29

recent and old, and we have ascertained that a good pharmaceutical grade glass, in the standard conditions of the above-described determination, has a maximum transfer of 60–70 μg of boric acid for 15 g of No. 35–55 powdered glass, obtained from ordinary ampoules. Finished and stamped pharmaceutical grade glass, used for antibiotic containers, yield even lower boric acid transfer values.

Typical data are summarized in Table II.

In conclusion, 1,8-dihydroxyanthraquinone permits the evaluation of boric acid in glasses and the determination of limit characteristics for a good grade product suitable for pharmaceutical use, as established by the following tests.

Qualitative test. A change in color of quinalizarin reagent, under the standard conditions, of over 50% of the ampoules or containers within 5 min can be tolerated. The Istizin reagent should not change color before 5 min.

Quantitative test. 15 g of glass powder under the standard conditions, should yield not more than 60–70 μg of boric acid, when Istizin is used as the reagent.

SUMMARY

1,8-Dihydroxyanthraquinone is proposed as an organic reagent for boric acid. The color change obtained is more useful for the determination of boric acid than those with other reagents of the anthraquinone group. The method is applied to the determination of boric acid transfers from pharmaceutical grade glass.

RÉSUMÉ

Le 1,8-dihydroxy-1,8-anthraquinone est proposée comme réactif pour l'identification et le dosage de l'acide borique, en particulier dans le verre destiné à des usages pharmaceutiques.

ZUSAMMENFASSUNG

Der Nachweis und zur Bestimmung von Borsäure, besonders in Glasbehälter für pharmazeutische Zwecke, wird die Reaktion der Borsäure mit 1,8-Dihydroxy-anthrachinon vorgeschlagen.

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APPLICATIONS DE LA CHÉLATOMÉTRIE

VI. DOSAGE VOLUMÉTRIQUE DES *vic*-DIOXIMES

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(Reçu le 10 décembre, 1960)

HISTORIQUE ET PRINCIPE

On connaît l'intérêt que les *vic*-dioximes présentent en chimie analytique minérale pour la détection et le dosage de plusieurs métaux. TSCHUGAEFF, le premier, puis BRUNK et, après eux, de nombreux autres ont décrit des méthodes gravimétriques, colorimétriques ou volumétriques de dosage du nickel, du palladium, du bismuth, du cobalt et du fer utilisant la diméthyl-glyoxime, la méthyl-éthyl-glyoxime, la méthyl-benzyl-glyoxime, les diphenyl-glyoximes ou "benzyl-dioximes", la difuryle-glyoxime et les cyclohexane, cycloheptane et cyclodécane-1,2 dioximes.

Les *vic*-dioximes présentent en outre des propriétés chimiques intéressantes en synthèse, ouvrant la voie notamment aux furoxannes ou oxadiazoles¹⁻⁸.

Peu de procédés ont été décrits pour l'estimation quantitative de ces réactifs; les seuls dont nous ayons connaissance reposent, soit sur une deshydrogénation au moyen de l'iode en présence d'un sel mercurique¹ — et cette dernière méthode présente le désavantage d'être perturbée en présence des monoximes des dicétones, et, d'une façon générale, en présence des oximes, lesquelles ont justement toutes les chances d'être rencontrées comme impuretés dans les dioximes — soit sur une gravimétrie au moyen d'un sel de nickel^{9,10}; le seul procédé volumétrique utilisant un sel de nickel consiste à redissoudre le dioximate dans un acide pour permettre le dosage de l'hydroxylamine après hydrolyse^{11,12} ce qui nécessite le transfert du précipité avec les inconvénients que comporte cette opération.

Nous avons préféré précipiter le dioximate par une quantité connue et en excès d'une solution d'acétate de nickel et après filtration, mesurer cet excès dans le filtrat en utilisant l'éthylène-diamino-tétracétate disodique ou "Chélate disodique" et la murexide qui nous avaient déjà donné satisfaction dans des travaux précédents^{13a,c}.

RÉACTIFS

Murexide à 1%

On pèse 0.1 g de murexide, ajoute 10 g de chlorure d'ammonium bien sec et broie le tout intimement au mortier.

Chélate disodique M/50

On pèse 7.4 g d'éthylène-diamino-tétracétate disodique qu'on dissout dans un peu d'eau distillée fraîchement bouillie et complète à un litre exactement avec cette

ème eau. On détermine la molarité de cette solution à partir d'un poids connu de magnésium ou de zinc métalliques chimiquement purs en utilisant le noir Eriochrome comme indicateur ou à partir d'une solution décimale de nitrate d'argent en présence de tétracyano-nickelate de potassium et de murexide¹⁴.

Chélate de nickel $M/5$

Dans 180 ml d'eau distillée on dissout 12.5 g de $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$; on complète 250 ml au moyen d'eau distillée. La molarité de la solution est mesurée de la façon suivante: On prélève au moyen d'une pipette 25 ml qu'on laisse couler dans une fiole jaugée de 250 ml et ajoute 50 ml d'ammoniaque; on complète jusqu'au trait de jauge avec de l'eau distillée; on agite pour homogénéiser la solution et prélève 25 ml (au moyen d'une pipette) qu'on laisse couler dans une fiole d'Erlenmeyer ou un bécher et auxquels on ajoute environ 0.3 g de murexide à 1%; on coule la solution de chélate préparée comme ci-dessus au moyen d'une burette jusqu'au virage au pourpre; la molarité est donnée par la formule:

$$N'_n = \frac{V_c \cdot N'_c}{2.5}$$

à V_c = nombre de ml de solution de chélate utilisés et N'_c = molarité de la solution de chélate.

MODE OPÉRATOIRE

On pèse un poids p de dioxime* qu'on place dans une fiole d'Erlenmeyer et on ajoute 10 ml d'ammoniaque; on porte à très légère ébullition puis ajoute 25 ml mesurés exactement de solution $M/5$ d'acétate de nickel; après quelques minutes d'ébullition on laisse reposer pendant une heure, on transvase dans une fiole de 250 ml en rinçant soigneusement à l'eau distillée et complète jusqu'au trait de jauge. On filtre sur papier ou sur creuset et prélève 25 ml avec une pipette; on ajoute environ 0.3 g de murexide à 1% et coule le chélate disodique au moyen d'une burette jusqu'à fin de virage au pourpre.

L'indimole de *vic*-dioxime^{13b} ou nombre de mmoles de *vic*-dioxime contenu dans 100 g de substance est calculé au moyen de la formule:

$$D_x = \frac{V \cdot 200}{p}$$

à $V = (25 \cdot N'_n) - (10 \cdot N'_c \cdot V')$, V' = nombre de ml de chélate $M/50$, N'_n = molarité de la solution d'acétate de nickel et N'_c = molarité de la solution de chélate.

Le titre % en *vic*-dioxime peut être établi au moyen de la formule:

$$T = \frac{D_x \cdot M_T}{1000}$$

M_T = masse moléculaire calculée de la dioxime essayée.

On calcule p de façon à consommer 40 à 50% de nickel.

RÉSULTATS OBTENUS

La présente méthode a été expérimentée sur quelques *vic*-dioximes soigneusement recristallisées; le Tableau I indique les résultats que nous avons obtenus.

TABLEAU I

<i>Echantillons dosés</i>	<i>Poids utilisé</i>	<i>Indimole théorique</i>	<i>Indimole trouvé</i>	<i>Titre trouvé</i>
Diméthylglyoxime	0.487	861	854	99.2
	0.492	861	856	99.4
	0.508	861	859	99.8
	0.502	861	853	99.1
Méthyléthylglyoxime	0.572	768	771	100.4
	0.580	768	765	99.6
	0.564	768	770	100.3
	0.575	768	765	99.6
Cyclohexane-1,2-dione-dioxime (nioxime)	0.634	703	705	100.3
	0.642	703	707	100.5
	0.638	703	704	100.2
	0.650	703	701	99.7
Di-furilglyoxime (furildioxime)	0.907	450	454	100.8
	0.918	450	451	100.2
	0.952	450	451	100.2
	0.930	450	453	100.6
Diphénylglyoxime (benzyldioxime)	1.140	416	412	99.1
	1.134	416	412	99.1
	1.142	416	415	99.8
	1.158	416	413	99.3

RÉSUMÉ

Les *vic*-dioximes peuvent être dosées facilement par précipitation au moyen d'un sel de nickel dont on mesure l'excès volumétriquement par chélatométrie.

SUMMARY

Vic-dioximes can be easily determined by precipitation with a nickel salt, excess of which is titrated with EDTA.

ZUSAMMENFASSUNG

Die quantitative Bestimmung von *vic*-Dioximen kann durch Fällung mit einer gemessenen Menge Nickelsalzlösung erfolgen, deren Überschuss mit EDTA titriert wird.

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A NEW REAGENT FOR THE DETECTION AND GRAVIMETRIC DETERMINATION OF SODIUM

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INTRODUCTION

With the exception of the triple uranyl acetate salts there are few satisfactory weighing forms for sodium. Other inorganic reagents have been recommended, but these have never been able to compete with the uranyl acetate reagents. In the field of organic reagents, dihydroxytartaric acid has received some attention, but the reagent is unstable and its sodium salt is rather too soluble for general application as a weighing form for sodium. Recently, α -methoxyphenylacetic acid^{1,2} and the magnesium salt of 8-aminonaphthalene-1-sulphonic acid^{3,4} have been recommended for the gravimetric determination of sodium. As these communications were published during the course of the present study⁵, which was concerned with the development of organic precipitants for the alkali metals, particularly sodium and potassium, we have felt it appropriate to include our own observations on these reagents.

α -Methoxyphenylacetic acid is not in our experience as sensitive for sodium as claimed¹. The lowest concentration of sodium to give a positive test is 3.3 mg sodium per ml of test solution. This compares very unfavourably with the uranyl acetate reagents. It is, however, more selective than zinc or magnesium uranyl acetate in that quite large concentrations of lithium do not interfere with its use. The precipitate given by this reagent is apparently an acid double salt of composition $C_6H_5CH(OCH_3) \cdot HOH \cdot C_6H_5CH(OCH_3)COONa$. Our results on 50-mg amounts of sodium show a negative error of 5–7%, the magnitude of which increases with a decrease in the amount of sodium present. The published procedure² involves the use of several different empirical correction factors which are applied in different circumstances; this seriously detracts from the use of the reagent for precise analytical work. We have also found that substitution in the active centre of the molecule of α -methoxyphenylacetic acid leading to compounds such as α -ethoxyphenylacetic acid, α -methoxydiphenylacetic acid, and α -methoxyfurylacetic acid destroys completely the property associated with the parent compound of forming a sparingly soluble sodium salt⁵.

The work of DRANITSKAYA³ on 1-aminonaphthalene-8-sulphonic acid is of greater significance. The magnesium salt of this acid is sufficiently soluble in water to allow the use of a 10% solution as the reagent. A three-fold excess of the reagent is necessary and the sodium salt is precipitated from a solution containing about 50% of ethanol. Details are given of the amounts of sodium determined, although this reagent is

later used⁴ for the detection of sodium at a limiting dilution of 1 in 4,000, equivalent to a concentration of 0.25 mg of sodium per ml. The reagent can tolerate potassium, ammonium and lithium in amounts up to about four-fold in excess of that of sodium.

Our studies of naphthylaminesulphonic acids have shown that of the common acids only the 1:8-acid has the properties reported by DRANITSKAYA and even this acid relies on a high reagent concentration and the presence of ethanol to precipitate sodium. It is not as sensitive as the uranyl acetate reagents.

New reagents examined

Numerous reports are found in the chemistry of the anthraquinonesulphonic acids of sparingly soluble alkali metal salts, yet no serious attempt has been made to apply the reactions of these acids for the detection and determination of the alkali metals. In a study of the derivatives of anthraquinone which are reported as having sparingly soluble alkali salts, only one compound has been found to have a sodium salt of sufficiently low solubility for possible analytical application. This compound, 5-benzaminoanthraquinone-2-sulphonic acid, was originally prepared by CLAUS⁶ in 1882 to characterise 5-aminoanthraquinone-2-sulphonic acid. He remarks that the sodium salt of this benzoyl derivative is very difficultly soluble in water.

We have now examined this compound and its precursor, 5-aminoanthraquinone-2-sulphonic acid, and find that the sodium salt of the latter is extremely soluble in water whereas the salt of the benzoyl derivative is not. Moreover, this low solubility is associated largely with the benzoyl group. Acylation of the amino-acid with acetyl and propionyl chlorides results in compounds with only moderate sensitivities to sodium: the trifluoroacetyl derivative is much more sensitive, but is not as sensitive as the benzoyl derivative. Isomers of 5-benzaminoanthraquinone-2-sulphonic acid have now been prepared and their reactions with sodium are compared by means of sensitivity determinations carried out under similar conditions. The compounds examined are given in Table I. 5-Trifluoroacetylanthraquinone-2-sulphonic acid is included for comparison.

TABLE I

Compound Anthraquinone	Sensitivity to sodium (mg per ml)	
	1-SO ₃ H	2-SO ₃ H
3-Benzamino	not prepared	15 ^a
5-Benzamino	2	0.10
8-Benzamino	20	12
5-Trifluoroacetyl	not prepared	0.30

^a This compound is the only one which shows a greater sensitivity to potassium, namely 2 mg/ml.

Of the five isomeric compounds, only 5-benzaminoanthraquinone-2-sulphonic acid is worthy of further study. When an aqueous ethanolic solution of this acid is added to an aqueous solution of sodium chloride, precipitation of the sodium salt is not instantaneous, even at concentrations as high as 5 mg per ml. Within 10–60 sec, however, depending on the concentration of sodium, precipitation of the shimmering orange-yellow sodium salt begins and continues until all the sodium in the solution has been consumed. Examination of this precipitate has shown it to have the expected

molecular formula, $C_{21}H_{12}NO_6SNa$ (by elemental analysis). It is very sparingly soluble in water, almost insoluble in ethanol, and insoluble in ether. On the basis of the molecular formula, it contains 5.358% of sodium.

Determination of the sensitivity of 5-benzaminoanthraquinone-2-sulphonic acid towards the alkali metals and the ammonium ion shows that the reagent, although lacking in selectivity, is extremely sensitive to the sodium ion. In the test procedure used, the reagent can detect 0.005 mg of sodium in a total volume of 2 ml, *i.e.* at a dilution of 1 in 400,000. Results are given in Table II, following the procedure described in the experimental section.

TABLE II

Ion	Sensitivity (mg/ml of ion present)
Li ⁺	0.60
Na ⁺	0.0025
K ⁺	0.28
Rb ⁺	0.10
Cs ⁺	0.08
NH ₄ ⁺	0.25

TABLE III

Sodium taken (mg)	Wt. of ppt. (mg)	Sodium found (mg)	Error %
1.40	24.5	1.32	-5.7
2.90	52.2	2.80	-3.5
4.30	79.8	4.28	-0.46
5.70	106.5	5.71	+0.17
8.60	160.4	8.60	0.00
10.00	186.7	10.00	0.00
11.50	214.2	11.48	-0.17
14.30	268.6	14.39	+0.62
17.20	322.6	17.28	+0.46
20.20	382.1	20.45	+1.24
22.80	426.6	22.86	+0.26
25.00	465.2	24.90	-0.40

The data show that the reagent is most sensitive to sodium, the sensitivity then decreasing in the order caesium, rubidium, ammonium, potassium, and lithium. The high sensitivity to sodium indicates that under the experimental conditions the precipitation of sodium must be complete for most practical purposes. Several quantitative experiments were therefore carried out in order to assess the suitability of the reagent for the gravimetric determination of sodium.

The most satisfactory conditions for the precipitation have now been established as (1) the presence of an 80-100% excess of the reagent, (2) a content of 50% of ethanol in the test solution, and (3) a standing time of 30 min for the ageing of the precipitate. The ethanol converts the initial microcrystalline precipitate into fine, easily filtered, crystalline needles. The sodium salt possesses a very favourable gravimetric factor, 0.05358. Table III lists some results obtained following the procedure described in the experimental section.

These results show that the reagent is quite satisfactory for the gravimetric determination of sodium. The relatively high errors in the determination of the lower amounts of sodium are due to the collection of the precipitate in a macro-crucible with consequent lack of precision. For amounts of sodium below 4 mg it would be better to use the techniques of micro-filtration.

The lower sensitivity of the reagent to potassium might have enabled its application for the determination of sodium in the presence of potassium, provided that most of the latter was removed, for example, as perchlorate. Solutions of sodium ion containing varying amounts of potassium not exceeding a concentration of 0.2 mg of potas-

sium per ml were analysed by the prescribed method. The results obtained were invariably high indicating that co-precipitation or induced precipitation of the potassium salt occurred. No further work on possible separations of sodium from potassium was done.

EXPERIMENTAL

(A) Preparation of reagent

Anthraquinone-2-sulphonic acid was nitrated according to the method of FIERZ-DAVID⁷ to give 5-nitroanthraquinone-2-sulphonic acid in 40% yield. This compound (10 g) was dissolved in the minimum quantity of boiling water and the hot solution was treated with a solution of sodium sulphide (200 ml; 20%) and sodium hydroxide (40 ml; 30%). The mixture was boiled for a few minutes, then cooled and filtered. The residue was dissolved in sufficient hot water and the solution was filtered to remove sulphur. The blood-red filtrate containing the sodium salt of 5-aminoanthraquinone-2-sulphonic acid was treated with concentrated hydrochloric acid (20 ml) which precipitated the free acid as silver-grey spangles. This was filtered off, and purified by re-precipitation from a solution of the sodium salt. (Yield 4.5 g, 50%. No m.p.). 5-Aminoanthraquinone-2-sulphonic acid (3 g) was dissolved in a mixture of pyridine (3 g) and nitrobenzene (15 g) and treated with benzoyl chloride (3 g). The mixture was heated under reflux at 156° for 0.5 h with continuous stirring.

The golden yellow crystalline needles which formed on cooling the mixture were filtered off, drained by suction, and washed with a small quantity of ether. The air-dried material was dissolved in warm ethanol (200 ml; 40%) and the solution was treated with a solution of sodium chloride (20 ml; 6%). The orange-yellow precipitate was filtered off, washed with cold water and suspended in the minimum quantity of hot hydrochloric acid (1 N). The salt slowly dissolved and on cooling the solution, the free acid separated as a fine, yellow, crystalline powder. This was filtered off, washed first with a little hydrochloric acid, then with water and finally air-dried. (Yield 2.0 g, 50%. m.p. 162°d).

(B) Determination of sensitivity of the reagent towards the alkali metals and ammonium Reagent solution

3% solution of 5-benzaminoanthraquinone-2-sulphonic acid in 50% aqueous ethanol. The solution is filtered and stored in a hard glass bottle. The stored solution reacts slowly with the alkali of the glass to give a precipitate, which must be filtered off before the solution is used. Alternatively, a polyethylene bottle can be used.

Alkali metal solutions

Solutions containing 1 mg/ml of alkali metal ion were prepared by dissolving the appropriate weight of the pure dry chlorides in water.

Test procedure

1 ml of the alkali metal solution contained in a small test tube was mixed with 1 ml of the reagent solution. The tube was stoppered and the contents were shaken for

1 min. The tube was set aside for 10 min, and examined for the appearance of a precipitate. The tests were repeated with progressively diluted solutions of each alkali metal until no precipitate was observed after 10 min from the time of mixing the reagent and test solutions.

(C) *Gravimetric determination of sodium*

Reagent solution

As in (B).

Procedure

1-10 mg of sodium. Pure, dry sodium chloride (or an aliquot of a solution of sodium chloride in water) was transferred to a 50-ml beaker. The salt was dissolved in 5 ml of water (or the solution concentrated or diluted to approximately 5 ml) and 5 ml of ethanol were added, followed by 15 ml of the reagent. The mixture was set aside for 30 min at room temperature and was stirred occasionally during this period. The precipitate was filtered off on a dry, weighed glass filter (porosity 4) and was washed successively with 3 1-ml portions of ethanol, 6 1-ml portions of ethanol saturated with the sodium salt, and finally with 4 1-ml portions of dry diethyl ether. Air was drawn through the precipitate for 5 min and the filter was then placed in a drying oven at 110°-120° and dried to constant weight (a time of about 30 min sufficed).

10-25 mg of sodium. The above procedure was used except that a 100-ml beaker was required and the volume for precipitation was increased from 10 ml to 20 ml in a solution approximately 50% with respect to ethanol; 30 ml of reagent were added. The washing and subsequent treatment of the precipitate were as described above. The theoretical factor is applicable. Thus, the percentage of sodium is given by:

$$\frac{\text{Wt. of precipitate (mg)} \cdot 5.358}{\text{Wt. of sample (mg)}}$$

(D) *Recovery of reagent*

The filtrates and precipitates from each determination were collected in a suitable vessel and sufficient of a solution of sodium chloride was added to precipitate all the excess reagent as the sodium salt. This was filtered off and treated as described in the section above dealing with the purification of the reagent.

DISCUSSION

5-Benzaminoanthraquinone-2-sulphonic acid is an extremely sensitive reagent for sodium ions. It is eight to ten times more sensitive than the uranyl acetate reagents. However, its lack of selectivity is a serious disadvantage for many analytical purposes. Although it is a satisfactory reagent for sodium, other alkali metals even in small amounts must be absent.

The relationship between molecular structure and precipitation of alkali metal salts is obscure. Of five isomeric compounds, only one exhibits this remarkable behaviour. It is difficult to understand why this particular orientation of substituents in the anthraquinone molecule produces this effect. Steric factors would not seem to be involved, because of the remoteness of the benzamino-group from the active salt-

forming sulphonic acid group. The similarity of the compounds containing the benz-amino- and trifluoroacetyl groups might indicate an electronic effect associated particularly with the 2:5-substitution. This particular orientation must give rise during salt formation to a crystal lattice of low energy compared with the lattice energies of the salts of the other derivatives. X-ray diffraction patterns have been obtained for the sodium salts of the six compounds listed in Table I. Each compound has a different diffraction pattern, and thus a different crystal structure. There is no evidence from the X-ray investigation that a chemical similarity exists among all six compounds.

In presenting the details of this new reagent, the authors have had to consider whether its possible applications in analysis are sufficient to justify publication; for there would seem to be little purpose in adding yet another useless reagent to the already overburdened literature on the analytical chemistry of the alkali metals. It is felt, however, that the existence of such a sensitive reagent should be made known. There are indications that further studies in the separation of the alkali metals by techniques such as ion-exchange may overcome the difficulties associated with the non-selectivity of the reagent; the accurate determination of sodium in the presence of other alkali metals would then become simple.

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SUMMARY

5-Benzaminoanthraquinone-2-sulphonic acid is recommended as a reagent for the precipitation of sodium. It is the most sensitive precipitant for sodium yet proposed, being able to detect 5 μg of sodium at a limiting dilution of 1 in $4 \cdot 10^5$. The reagent is not selective and is unable to tolerate the presence of the other alkali metals and the ammonium ion. The use of the reagent for the gravimetric determination of 1.40–25.0 mg of sodium is described.

RÉSUMÉ

Un nouveau réactif, l'acide benzamino-5-anthraquinone sulfonique-2, est proposé pour l'identification et le dosage gravimétrique du sodium. Cette réaction est très sensible, mais pas sélective; les autres métaux alcalins et l'ammonium gênent.

ZUSAMMENFASSUNG

Als neues, sehr empfindliches Fällungsreagenz für die Bestimmung von Natrium wird die 5-Benzamino-anthrachinon-2-sulfosäure empfohlen. Die anderen Alkalimetalle und Ammonium-Ionen stören und müssen vorher entfernt werden.

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ANALYSE THERMOGRAVIMÉTRIQUE DE QUINALDATES MÉTALLIQUES

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Au cours d'un travail d'ensemble effectué sur les chélates métalliques de l'acide picolique (pyridine 2-carboxylique)¹ nous avons montré l'utilité de l'analyse thermogravimétrique des produits cristallisés pour déterminer la constitution des chélates, leur taux d'hydratation, la stabilité thermique des molécules d'eau fixées, celle des produits anhydres, et les conclusions intéressantes qu'on pouvait en déduire sur la structure des chélates^{2,3}.

Une étude parallèle a été poursuivie sur les chélates de l'acide quinaldique (quino-
léine 2-carboxylique). Les résultats obtenus font l'objet de la présente communication.

DÉTAILS EXPÉRIMENTAUX

(1) *Préparation des quinaldates*: La présente étude est limitée aux cations suivants: alcalino-terreux Mg, Ca, Ba, et cations bipoitifs lourds Cu, Pb, Mn, Cd, Hg, Zn, Ni, Co, Fe.

L'acide quinaldique utilisé était un produit commercial que nous avons purifié par recristallisation dans le benzène.

Les quinaldates alcalino-terreux sont préparés par neutralisation de la solution d'acide par le carbonate correspondant.

Les quinaldates de cuivre, plomb, manganèse, cadmium, mercure, zinc, nickel, s'obtiennent facilement par addition d'une solution de quinaldate de sodium à une solution du sel métallique correspondant; leur filtration et leur séchage sont facilités si on opère en milieu acétique et à chaud; par exemple, le quinaldate de nickel préparé dans ces conditions correspond à un hydrate bien défini à 2 molécules d'eau, alors que le mélange des deux solutions neutres à froid conduit sensiblement à un trihydrate dont une molécule d'eau s'élimine progressivement par un séchage prolongé à l'air sur creuset filtrant en donnant le dihydrate stable.

Deux quinaldates de cobalt différents avaient déjà été préparés par DUTT⁴: l'un, de couleur crème, est obtenu en milieu neutre, l'autre, rose-rouge, en milieu acétique. Ces deux composés, nous les avons également obtenus suivant les indications de DUTT. D'autre part, à partir d'une solution de sel de Mohr contenant 1% de chlorhydrate d'hydroxylamine, nous avons préparé deux variétés définies de quinaldates ferreux: (a) par addition de 100 ml d'une solution 0.1 M d'acide quinaldique à 50 ml d'une solution 0.1 M chaude du sel de Mohr, il se forme, après une intense coloration rouge, un précipité rouge qui est rapidement filtré et lavé à chaud; (b) en ajoutant à 50 ml de la solution froide 0.1 M de sel de Mohr 100 ml d'une solution 0.1 M de quinaldate de sodium, on obtient un précipité violet que l'on filtre et lave à froid.

Tous les quinaldates ont été filtrés sur creusets filtrants no. 3 ou 4, lavés et séchés par aspiration d'air un minimum de 24 h.

(2) *Analyse thermogravimétrique*: L'étude a été effectuée à l'aide de la thermobalance de Chevenard, en atmosphère ordinaire, sur un poids initial moyen de 300 mg.

Une perte de poids de 200 mg correspond à 155–156 mm sur le papier photographique. Les taux d'hydratation sont déterminés par mesure, sur la courbe, de la hauteur du premier palier; on calcule le poids correspondant, rapporté au poids total de précipité, pesé dans son creuset avant et après l'opération. Si la perte d'eau ne se manifestait sur la courbe que par une variation de 8 à 10 mm, on effectuait, pour plus de précision, un autre enregistrement, sur un poids plus important, en fixant la température maximum à celle correspondant au produit du palier anhydre.

Nous avons utilisé le même régime de température que pour les picolates: montée linéaire de 3 degrés environ par min, jusqu'à 700° et maintien 2 h à cette température. C'est le même régime thermique qu'ont utilisé BORREL ET PÂRIS⁵ pour leur étude des oxinates et des méthyl-2 oxinates⁶ et BOCQUET ET PÂRIS⁷ pour l'étude des phényl-2 oxinates.

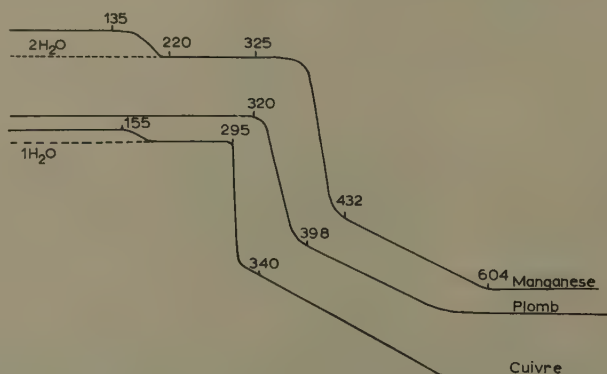


Fig. 1. Thermogravimétrie des quinaldates de cuivre, de manganèse et de plomb.

Les formules des quinaldates sont établies en comparant les pourcentages de métal et d'eau expérimentaux avec les pourcentages théoriques, compte tenu de la nature du résidu: MgO, BaCO₃, CaO (dans ce cas, la montée linéaire de 3° par min a été poursuivie jusqu'à 1000°), CuO, PbO, CdO, ZnO, NiO, Co₃O₄, Fe₂O₃. Dans certains cas, le métal a dû être dosé directement sur le quinaldate après minéralisation: Mg, Mn, Fe, comme il est indiqué sur les Tableaux I et II.

RÉSULTATS

Nos courbes sont reproduites dans les Figs. 1, 2, 3, et 4. Elles présentent toutes la même allure caractéristique pour la décomposition du chélate, allure que nous avons déjà signalée pour les picolates: perte de poids brutale suivie d'un net changement de pente. Pour les quinaldates de cuivre et de nickel, cette décomposition est même explosive. La décomposition peut conduire au métal, avec les quinaldates de cobalt et nickel (Fig. 3).

Les Tableaux I et II résument les résultats obtenus; t_1 est la température de début de déshydratation du quinaldate, t_2 la température de début de décomposition

du chélate anhydre. Elles correspondent aux points où la courbe quitte l'horizontale.

En ce qui concerne la composition des différents quinaldates examinés, la littérature fournit plusieurs références sur les quinaldates monohydratés de cuivre⁸⁻¹⁴, zinc^{8,15-20} et cadmium¹², leur insolubilité permettant de les utiliser pour le dosage de ces cations, seuls, ou en présence d'autres ions dans des conditions déterminées.

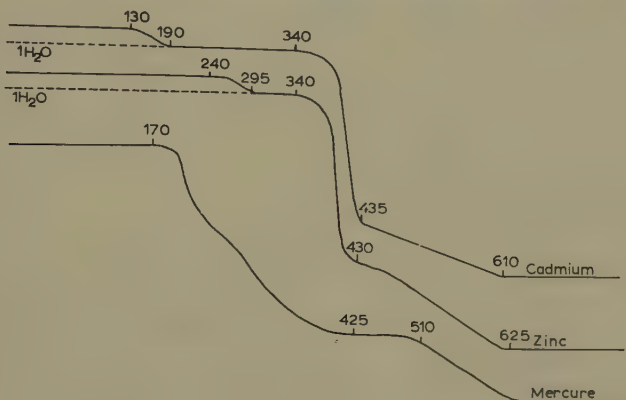


Fig. 2. Thermogravimétrie des quinaldates de cadmium, de zinc et de mercure.

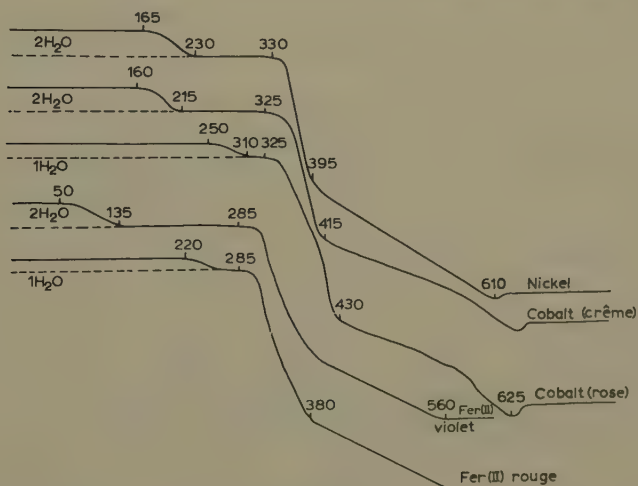


Fig. 3. Thermogravimétrie des quinaldates de nickel, de cobalt et de fer(II).

Les quinaldates de cobalt crème et rose-rouge préparés par DUTT⁴ sont décrits avec, respectivement 2 et 0 molécules d'eau, alors que nos résultats conduisent à 2 et 1 H₂O, cette molécule d'eau étant particulièrement solide (250°).

Le quinaldate ferreux violet, préparé par RÂV ET BOSE¹⁹ est décrit avec 5 H₂O. Celui que nous avons préparé contient 2 H₂O. Quant à la variété rouge que nous avons obtenue, sa composition correspondrait à Fe(C₁₀H₆O₂N)₂·H₂O, cette molécule d'eau étant également très solide (220°):

% théoriques pour Fe(C₁₀H₆O₂N)₂·H₂O; C : 57.44, H : 3.12, N : 6.70, Fe : 13.35.

trouvé; C : 57.38, H : 3.39, N : 6.50, Fe 13.37.

Au cours de la rédaction de cet article, nous avons eu connaissance du résumé d'un travail de LUMME²¹ concernant l'étude de la stabilité thermique des quinaldates des cations bipoitifs Cd, Co, Cu, Zn, Ni, Pb. Nous avons noté quelques divergences avec nos propres résultats, en particulier au sujet du nombre de molécules d'eau d'hydratation des chélates de nickel (l'auteur signale un trihydrate et un monohydrate) et de zinc (l'auteur signale un tétrahydrate).

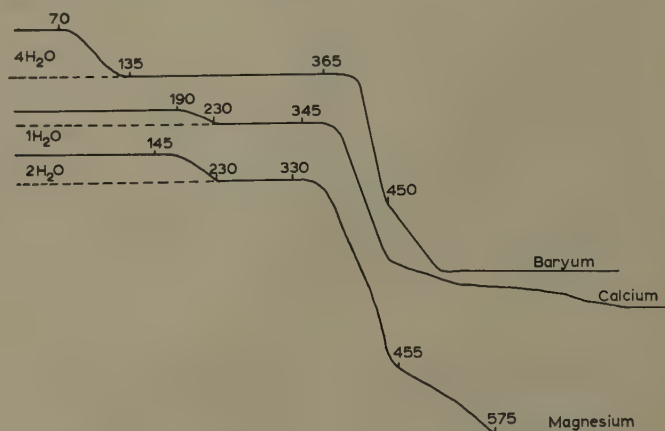


Fig. 4. Thermogravimétrie des quinaldates alcalino-terreux.

TABLEAU I
QUINALDATES DE CATIONS ALCALINO-TERREUX

Quinaldate	Couleur	t_1	t_2	% métal		% H_2O	
				expér.	théor.	expér.	théor.
$Mg(C_{10}H_6O_2N)_2 \cdot 2H_2O$	blanc	145		6.14 ^a	6.01	8.7	8.90
$Mg(C_{10}H_6O_2N)_2$			330	6.50	6.60		
$Ca(C_{10}H_6O_2N)_2 \cdot H_2O$	blanc	190		10.04 ^b	9.96	4.55	4.47
$Ca(C_{10}H_6O_2N)_2$			345	10.52	10.42		
$Ba(C_{10}H_6O_2N)_2 \cdot 4H_2O$	blanc	70		24.65 ^c	24.81	13.2	13.01
$Ba(C_{10}H_6O_2N)_2$			365	28.40	28.51		

^a Dosé sur le quinaldate après minéralisation par le complexe III.

^b Calculé d'après le résidu CaO obtenu par chauffage à 1000°.

^c Calculé d'après le résidu BaCO₃.

CONCLUSIONS

(I) Stabilité thermique des quinaldines anhydres

Nous avons représenté sur la Fig. 5 les températures t_2 de début de décomposition des quinaldates anhydres, données dans les Tableaux I et II ainsi que les températures correspondantes des oxinates⁵ et des picolates¹. Nous constatons que les stabilités thermiques sont du même ordre de grandeur, les quinaldates ayant, en général, une stabilité intermédiaire entre celles de l'oxinate et du picolate correspondants. En outre, la variation de t_2 en fonction de la nature de cation donne pour les 3 réactifs des séries sensiblement parallèles, les quinaldates se situant entre les oxinates et les picolates. Comme l'avaient noté BOCQUET ET PÂRIS⁷: l'ordre des stabilités thermiques est l'inverse de l'ordre des stabilités ioniques.

TABLEAU II
 QUINALDATES DE CATIONS BIPOSITIFS LOURDS

Quinaldate	Couleur	t_1	t_2	% métal		% H ₂ O	
				expér.	théor.	expér.	théor.
Cu(C ₁₀ H ₆ O ₂ N) ₂ · H ₂ O	bleu-vert	155		14.88	14.92	4.25	4.23
Cu(C ₁₀ H ₆ O ₂ N) ₂			295	15.55	15.58		
Pb(C ₁₀ H ₆ O ₂ N) ₂	blanc		320	37.55	37.57		
Mn(C ₁₀ H ₆ O ₂ N) ₂ · 2H ₂ O	blanc jaunâtre	135		12.74 ^a	12.62	8.2	8.27
Mn(C ₁₀ H ₆ O ₂ N) ₂			325	13.87 ^a	13.75		
Cd(C ₁₀ H ₆ O ₂ N) ₂ · H ₂ O	blanc	130		23.54	23.67	4.0	3.80
Cd(C ₁₀ H ₆ O ₂ N) ₂			340	24.65	24.61		
Hg(C ₁₀ H ₆ O ₂ N) ₂	blanc		170				
Zn(C ₁₀ H ₆ O ₂ N) ₂ · H ₂ O	blanc	240		15.28	15.29	4.4	4.21
Zn(C ₁₀ H ₆ O ₂ N) ₂			340	15.98	15.95		
Ni(C ₁₀ H ₆ O ₂ N) ₂ · 2H ₂ O	vert-bleu	165		13.47	13.37	8.36	8.20
Ni(C ₁₀ H ₆ O ₂ N) ₂			330	14.70	14.56		
Co(C ₁₀ H ₆ O ₂ N) ₂ · 2H ₂ O	crème	160		13.40	13.42	8.35	8.20
Co(C ₁₀ H ₆ O ₂ N) ₂			325	14.60	14.61		
Co(C ₁₀ H ₆ O ₂ N) ₂ · H ₂ O	rose rouge	250		13.93	13.99	4.25	4.28
Co(C ₁₀ H ₆ O ₂ N) ₂			325	14.55	14.61		
Fe(C ₁₀ H ₆ O ₂ N) ₂ · 2H ₂ O	violet	50	285	12.76 ^a	12.80	8.4	8.26
Fe(C ₁₀ H ₆ O ₂ N) ₂				13.94	13.95		
Fe(C ₁₀ H ₆ O ₂ N) ₂ · H ₂ O	rouge	220	285	13.37 ^a	13.35	4.4	4.30

^a Dosages effectués sur le chélate après minéralisation, dosage du manganèse par le complexe III et du fer par le bichromate.

(2) Nombre et stabilité des molécules d'eau dans les quinaldates cristallisés

Nous avons rassemblé dans le Tableau III le nombre de molécules d'eau, et les températures de déshydratation correspondantes des chélates de l'acide quinaldique, de l'acide picolique, et de l'oxine.

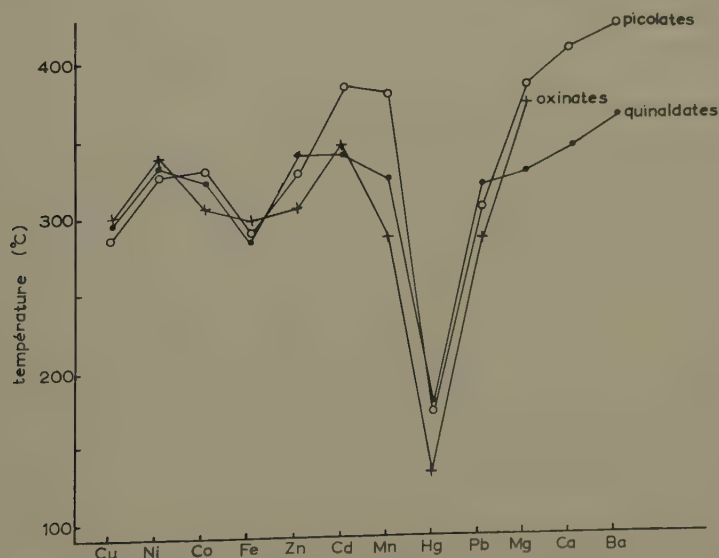


Fig. 5. Décomposition thermique des chélates anhydres. quinaldates; ○○○○ picolates; +++ oxinates.

Dans notre étude antérieure sur les picolates métalliques^{1,3} nous avons déduit, de l'examen de la stabilité des molécules d'eau d'hydratation des picolates et des oxinates, une structure possible pour les chélates cristallisés: 2 molécules d'agent chélatant fixées sur un ion métallique bipoitif satisfont une coordinence de 4. Si deux molécules d'eau restent également fixées sur le cation, donc solidement, la coordinence est 6 et la structure probable octaédrique; si les molécules fixées le sont faiblement, on peut avancer l'hypothèse d'une coordination limitée à 4.

TABLEAU III
NOMBRE DE MOLÉCULES D'EAU DES CHÉLATES

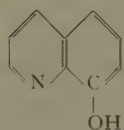
	Cd	Hg	Cu	Pb	Zn	Mn	Ni	Co	Fe	Mg	Ca	Ba
Quinaldate	1 130	0	1 155	0	1 240	2 135	2 165	$\begin{cases} 2 \\ 160 \\ 1 \\ 250 \end{cases}$	$\begin{cases} 2 \\ 50 \\ 1 \\ 220 \end{cases}$	2 145	1 190	4 70
Picolate	0	0	2 50	2 50	4 70	2 100	4 75-145	4 75-145	4 75-145	2 145	1 155	0
Oxinate	2 116	0	2 60	0-2 45	2 70	2 117	2 120	2 115	2	2 122		
Méthyl-oxinate	0	1	1 112	1.3 45	1 128	1 125	1 215	1 152		1 134		

Si nous comparons les résultats obtenus pour les quinaldates avec ceux précédemment obtenus pour les picolates et oxinates, nous constatons:

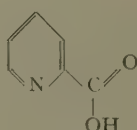
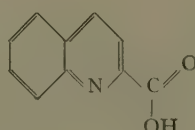
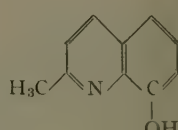
Les quinaldates de plomb et mercure sont anhydres; on pourrait leur attribuer une structure tétraédrique comme aux picolates et aux oxinates qui sont soit anhydres, soit hydratés à 2 molécules d'eau faiblement liées.

Les quinaldates de manganèse, nickel, cobalt, magnésium ont deux molécules d'eau solidement fixées, comme les oxinates correspondants et comme les picolates, si on ne considère comme solides que les molécules d'eau qui s'éliminent au dessus de 100°; on peut donc, pour les quinaldates de ces cations, envisager une structure octaédrique, comme pour les autres chélates examinés.

Les picolates de cuivre, zinc n'ont que deux molécules d'eau faiblement liées; celui de cadmium est anhydre. Or, les quinaldates correspondants ont tous une molécule d'eau, molécule qui est particulièrement solide. Il nous semble difficile dans ce cas, de faire des déductions valables concernant les structures à partir de ces seuls résultats d'analyse thermogravimétrique.



Oxine

Acide
picoliqueAcide
quinaldique

Méthyl 2-oxine

L'environnement du groupement chélatant dans la molécule de l'acide quinaldique est plus encombré que pour l'acide picolique, ou l'oxine. Si nous reportons (Tableau

III) les hydrates des méthylloxinates, à titre de comparaison, nous constatons que ceux de cuivre et de zinc en particulier n'ont qu'une molécule d'eau, et que celle-ci est également solide. Nous pouvons penser que la présence d'une seule molécule d'eau d'hydratation dans ces chélates résulte d'un empêchement stérique.

Il serait naturellement nécessaire de déterminer de façon précise la structure de ces chélates hydratés par une analyse complète du cristal aux rayons X afin de connaître la position exacte des molécules d'eau dans le réseau. Nous ferons simplement remarquer pour l'instant que, lorsque ces structures seront connues, elles devront obligatoirement rendre compte de la solidité des molécules d'eau que notre analyse thermogravimétrique a permis d'établir de façon indiscutable.

RÉSUMÉ

Les auteurs déterminent par analyse thermogravimétrique le taux d'hydratation, la stabilité thermique des quinaldates anhydres, et la stabilité des molécules d'eau d'hydratation; des déductions possibles sont tirées en relation avec la structure, et par comparaison avec les résultats obtenus antérieurement avec les oxinates et picolates métalliques.

SUMMARY

Thermogravimetric analysis is used to determine the hydration of metallic quinaldates, as well as the thermal stability of the anhydrous quinaldates and of the water of hydration. Deductions are made with regard to structure by comparison with results previously obtained for oxinates and picolates.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Hydrate von Metallchinaldaten, thermische Stabilität der wasserfreien Chinaldaten und des Hydratwassers durch thermogravimetrische Analyse. Es werden Rückschlüsse auf die Struktur gezogen durch Vergleich mit den Oxinaten und Picolaten.

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A SENSITIVE NEW METHOD FOR THE DETERMINATION OF NITRITES AND NITROGEN DIOXIDE WITH 4-AMINOAZOBENZENE-1-NAPHTHYLAMINE

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INTRODUCTION

In previous work it has been shown that the di-cationic salts of N,N-dimethyl-*p*-(*p*-phenylazophenylazo)aniline type compounds are dark blue with a molar absorptivity of over 100,000 in strongly acid solution¹. Because of this easily visible color and the high order of sensitivity, analytical methods forming the same type of chromogen were developed for the detection and determination of aniline, naphthylamine and anthramine derivatives, as well as their N-alkyl and N,N-dialkyl analogues². However, unlike the aniline derivatives, 1-naphthylamines reacted readily with the reagent, 4-azobenzenediazonium fluoborate, at room temperature to give the intensely colored chromogen in practically quantitative yield. Hence it appeared that 4-aminoazobenzene and a 1-naphthylamine derivative would react readily with nitrous acid to give the intensely blue di-cation.

The determination of the nitrite ion through formation of an azo dye is a well-known method which has been recently reviewed³. The main advantage of the present procedure is its greater sensitivity.

The blue chromogen formed is the dication of 4-(*p*-phenylazophenylazo)-1-naphthylamine. It has a molar absorptivity of 93,000. This value compares favorably with the value of 95,000 obtained in the determination of 1-naphthylamine with 4-azobenzenediazonium fluoborate².

EXPERIMENTAL

Reagents and equipment. 4-Aminoazobenzene and 1-naphthylamine (both from Distillation Products Industries) were crystallized several times from pentane to give products melting at 130° and 50°, respectively.

Reagent solution. A solution of 0.02 g of 1-naphthylamine and 0.12 g of 4-aminoazobenzene in 40 ml of 2-methoxyethanol was diluted to 100 ml with water.

A Cary Model 11 recording spectrophotometer with 1-cm cells was used in the colorimetric determination.

Procedure I

The residue to be analyzed is dissolved in 5 ml of reagent solution diluted with 5 ml

of water. To this solution of sample and reagent is added 1 drop (0.03 ml) of concentrated hydrochloric acid. After 30 min hydrogen chloride gas is passed through for 5 min. During this latter process the temperature of the solution in the water-cooled tube rises from about 26° to about 84° in 2 min and then drops to approximately 24° at the end of the 5-min period. No precautions are taken to keep the temperature constant, as reproducible results are obtained without doing so. The mixture is then cooled to room temperature and diluted to 15 ml with 2-methoxyethanol. The absorbance of the solution at 643 m μ is then determined against a proper blank.

Procedure II

For the collection of nitrogen dioxide, air can be aspirated through 5 ml of 0.02 *N* sodium hydroxide solution, as described by JACOBS AND HOCHHEISER⁴. (In the presence of a large excess of sulfite ion one drop of 1% hydrogen peroxide is added, followed by a 5-min wait). 5 ml of the reagent solution is then added, followed by 2 drops (0.06 ml) of concentrated hydrochloric acid. The mixture is allowed to stand for 30 min. Then hydrogen chloride gas is passed through for 5 min. The mixture is cooled to room temperature and then diluted to 15 ml with approximately 6 *N* hydrochloric acid. The absorbance of the solution at 643 m μ is then determined against a proper blank.

DISCUSSION

Variables in *procedure I* were investigated. Holding all factors constant except the variable under study, 5 ml of a 0.000162% aqueous solution of sodium nitrite was analyzed. Increasing the concentration of 4-aminoazobenzene in the reagent solution increased the intensity (Fig. 1), which reached a maximum with 0.006 g of this

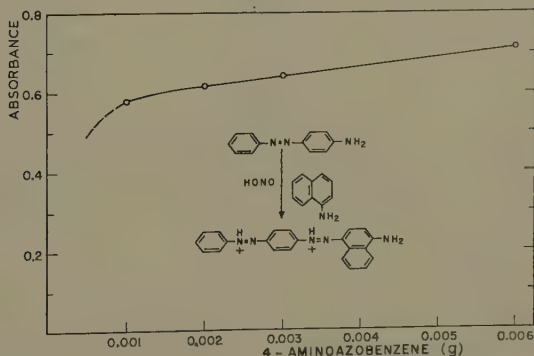


Fig. 1. Effect on absorbance of variation in the amount of 4-aminoazobenzene in 5 ml of the reagent solution containing 1 mg of 1-naphthylamine.

amine per 5 ml of reagent solution. Any greater concentration caused precipitation in the final colored solution. On the other hand a decrease in the amount of 1-naphthylamine in the reagent solution caused a slight increase in intensity throughout the range of amine concentrations investigated (Fig. 2). Use of 0.001 g of 1-naphthylamine per 5 ml of reagent solution gave optimum results; lower concentrations produced about the same intensity, but the higher concentration was preferred so

that larger quantities of nitrogen dioxide or nitrite ion could be handled. 1 drop (0.03 ml) of concentrated hydrochloric acid was found to speed up the reaction, but more acid gave no further improvement. A wait of 30 min gave optimum results. After waiting periods of 5 and 120 min, intensities were 2% and 10% lower than the optimum. Passage of hydrogen chloride gas through the solution was found necessary to obtain

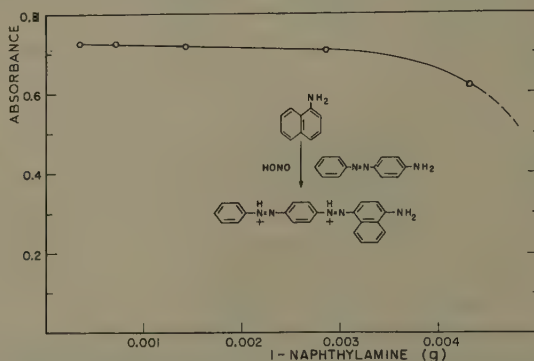


Fig. 2. Effect on absorbance of variation of 1-naphthylamine in 5 ml of the reagent solution containing 6 mg of 4-aminoazobenzene.

an essentially quantitative reaction, while passages of 3, 5 and 10 min gave exactly the same intensity. Final dilution of the solution with approximately 6 *N* hydrochloric acid instead of 2-methoxyethanol did not alter the absorbance of the solution. The color intensity was stable for at least 4 h; after 46 h the absorbance had dropped from an initial value of 1.10 to 0.52. For *procedures I* and *II*, Beer's law was obeyed from 0.5 to over 16 μg of nitrite ion per 15 ml of final solution (Fig. 3).

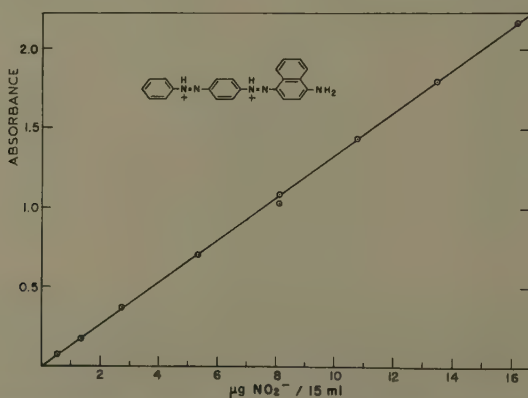


Fig. 3. Concentration-absorbance curve obtained in the spectrophotometric determination of nitrite ion.

N-methyl-1-naphthylamine and N-1-naphthylethylenediamine can be substituted for 1-naphthylamine.

Possible interferences were investigated. The nitrate ion, phenol, nitromethane, formaldehyde, acetone and aromatic nitroso compounds, such as nitrosobenzene and

,N-dimethyl-*p*-nitrosoaniline gave no blue color in the procedure when they were substituted for the nitrite ion. Nitrate, sulfate and chloride ion did not interfere with the determination of nitrite. To test the interference of sulfur dioxide or the sulfite ion, aqueous solutions of sodium metabisulfite were used. A concentration of the sulfite ion (or sulfur dioxide) twice that of the nitrite ion showed very little interference. However, in the presence of 35 times the concentration of sulfur dioxide the intensity obtained by both procedures was approximately halved. The sulfite ion probably interferes by reducing the diazonium salt formed from nitrous acid and 4-aminoazobenzene to a hydrazine which does not react with 1-naphthylamine to form the blue chromogen. However, as JACOBS AND HOCHHEISER⁴ have pointed out, this interference can be eliminated with the use of hydrogen peroxide, as shown in *procedure II*. In the case of a residue containing large amounts of sulfite, *procedure II* can be used by dissolving the residue in 5 ml of 0.02 *N* sodium hydroxide solution followed by treatment with a drop of 1% hydrogen peroxide, etc. With this procedure the interference of sulfite is eliminated to some extent.

SUMMARY

A sensitive method for the determination of nitrites is proposed. The method should also be applicable to the determination of nitrogen dioxide. The test consists of the reaction of 4-aminoazobenzene and 1-naphthylamine with nitrous acid to form the blue di-cation of 4-(*p*-phenylazo-phenylazo)-1-naphthylamine. Beer's law was obeyed from 0.5 to over 15 μg of nitrite ion per 15 ml of final solution. Spectrophotometrically it is possible to detect 1 part of nitrite ion in 60 million parts of solution.

RÉSUMÉ

Une méthode sensible est proposée pour le dosage colorimétrique des nitrites et du bioxyde d'azote. Elle est basée sur la coloration bleue, obtenue avec l'amino-4-azobenzène et l' α -naphthylamine.

ZUSAMMENFASSUNG

Beschreibung einer empfindlichen colorimetrischen Methode zur Bestimmung von Nitriten und Stickstoffdioxyd. Sie beruht auf der Bildung einer blauen Färbung mit 4-Aminoazobenzol und 1-Naphthylamin.

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A MODIFIED TRITIUM GAS COUNTING PROCEDURE

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The one-step method for tritium analysis¹ has been reported to give a high precision in counting reproducibility. The procedure consists in the quantitative conversion of tritium in organic compounds to a mixture of hydrogen and methane which is then expanded into an ionization chamber and the ion-current measured with a vibrating reed electrometer². Previous experience^{3,4} with the technique has proved that it is very satisfactory although some research workers have observed difficulty in the quantitative conversion of some organic compounds, particularly some halogenated derivatives^{2,5}.

The method of analysis can be divided into four operations:

- (a) Weighing the sample in solid or liquid form.
- (b) Conversion of the tritium in the sample into the gaseous state by combustion at approximately 640–675° in the presence of nickelic oxide and zinc catalysts.
- (c) Introduction of a definite aliquot of this gas into an ionization chamber, followed by dilution to approximately one atmosphere with counting gas such as methane.
- (d) Measurement of the ion current and therefore the activity in the chamber by means of a vibrating reed-recorder combination.

The error in the first operation can be minimized to less than 0.5% by using a micro-balance whilst that involved in the third and fourth operations is also less than 0.5%⁶. The accuracy of the analysis depends, therefore, to a large extent on the second operation and in this respect the nature of the zinc and nickelic oxide catalysts is of critical importance. Difficulty in obtaining satisfactory results with imported catalysts*, particularly zinc mesh, has prompted us to make a re-investigation of certain aspects of the procedure, particularly the possibility of using very active zinc dust instead of zinc mesh for the combustion.

It is the purpose of this paper to report the results of our investigation into the factors affecting the conversion so as to provide a modified method of high reproducibility. Such factors governing completeness of conversion include: (1) the surface area of the zinc; (2) absorption of the converted gases by the zinc and nickelic oxide; (3) temperature dependence of the diffusion of converted gases through the special glass combustion tube.

* WILZBACH *et al.*² stress the need to use zinc catalyst to the following specifications: "Baker's Analyzed" Blue Label 40 mesh, low in Pb and Fe. This gives satisfactory results but, unfortunately, only 20 mesh was available and this latter catalyst is not satisfactory as the results in this paper show.

EXPERIMENTAL

Materials used

Zinc (type 1), granular, 20 mesh, Baker & Adamson, low in Pb and Fe. *Zinc (type 2)*, zinc dust, superfine, kept under nitrogen and supplied by By-products & Chemicals Pty. Ltd., Sydney. *Nickelic oxide*, Baker & Adamson, black powder, nickel content 73%. *Combustion glass tubing*, special Pyrex 1720 glass, 1.3 cm I.D. and 1.8 cm O.D., from Corning Glass Works, N.Y. (U.S.A.). *Propane*, 99% purity obtained from Commonwealth Industrial Gases Ltd., Sydney. *t-Benzoic acid*, this was prepared using the WILZBACH technique⁷ by exposing 1 g of benzoic acid to 1 C of tritium gas for several weeks. The benzoic acid was recrystallized to radiochemical purity using methanol-water solvent systems. *t-Anthranilic acid*, anthranilic acid (0.5 g) was exposed to 3 C of tritium for two weeks. An aliquot (0.03 g) of this labelled anthranilic acid was diluted with carrier (1.0 g) and recrystallized from hot water to constant activity. In this step traces of phenolic materials could only be removed by alternately using small amounts of charcoal and activated aluminium oxide (Alumina Grade "H", Hopkin & Williams Ltd., England) in the recrystallizing solvent. Distribution experiments (GARNETT AND LAW⁸) with this *t*-anthranilic acid confirmed radiochemical purity.

Counting equipment

Vibrating Reed Electrometer, Cary Model 31, from the Applied Physics Corporation, California (U.S.A.) with the attached multiple leak resistor holder Model 309 and 250-cm³ Borkowski type ionization chambers.

Sampling techniques

Solids. Solid samples (approx. 5 mg) were weighed by difference in zinc boats (pressed from pure zinc sheet) using a microbalance to an accuracy of 0.002 mg.

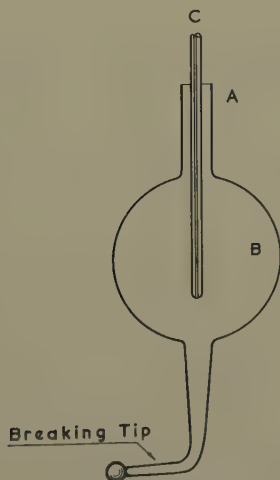


Fig. 1.

Liquids. Considerable time was spent in testing various alternatives for liquid sampling. In the original tritium analytical publication², sampling was achieved by

warming the carrier glass ampoule and allowing the sample to be sucked in as the ampoule cooled. The ampoule was then sealed and the sample weighed by difference. For studies utilizing a system of solvents, particularly volatile solvents (*e.g.* radio-metric titrations^{9,10}), evaporation caused by the hot glass ampoule introduces an appreciable error. The following procedure was found to give improved accuracy.

A glass ampoule as shown in Fig. 1 was made small enough to be placed in the combustion tube yet possessing a bulb B which was large enough to prevent creep of the liquid sample up the end A. The liquid sample was introduced by capillary C, the end A sealed and sample weighed by difference.

Analytical procedure

The published method² was followed as closely as possible. Variations in combustion procedure such as catalyst concentration, temperature, etc., are indicated in the pertinent tables. In general, samples were mixed with zinc and nickelic oxide catalysts in a special combustion tube fitted with a break-seal tip. The reaction tube was then constricted, evacuated to a pressure of less than 0.5 mm, sealed off and combusted in a furnace at approximately 640–675° for the required time (usually 1 h). Oven calibration was performed using a thermocouple which was standardized by C.S.I.R.O. National Standards Laboratory, Sydney. This indicated that the temperature gradient was less than 5° from one end to the other. After cooling to room temperature, the gases in the combustion tube were expanded into a 250-cm³ ion chamber which was then filled to one atmosphere with the counting gas, propane. Propane was used in this step due to the difficulty in obtaining adequate supplies of the recommended methane. The ion current in the chamber was measured by the technique of rate-of-charge of the capacitor rather than by the constant leak circuit which was not quite as accurate for the range of activities measured.

RESULTS AND DISCUSSION

In Table I, Series A, the effect of the surface area of the zinc on the conversion reaction using *t*-benzoic acid is reported. It can be seen that there is a marked increase in specific activity when the surface area of the zinc is increased. In those samples where granulated zinc was used, incomplete conversion was obtained. Reproducibility in triplicate samples using zinc dust was 2%, so that for the remainder of the studies reported in this paper, zinc dust was used* (*i.e.* Tables II and III).

From the data in Series B of the same table, it can be seen that there is both a decrease in the specific activity and overall reproducibility of the analysis as the proportion of nickelic oxide increases. This can be attributed to either absorption of the converted gases by the nickelic oxide catalyst surface or to a decrease in conversion efficiency of the zinc dust due to the dilution effect of excess nickelic oxide, although from our present evidence this second alternative appears to be unlikely.

The effect of varying the quantity of zinc dust used is reported in Series C. Below 0.5 g of zinc dust (for 0.1 g nickelic oxide) the conversion reaction is incomplete after combustion for three hours. For quantities of zinc dust in excess of this amount, there

* As these studies were being completed, SWAIN *et al.*³ also reported the necessity to use zinc dust instead of granulated zinc to obtain complete conversion. However, these authors did not report a detailed study of the analytical procedure using zinc dust catalyst at that time.

TABLE I
 VARIATION IN CATALYST CONDITIONS^a

Series	Purpose of experiment	Zinc		Nickelic oxide (g)	Sample size ^b (mg)	Specific activity (V/min/mg)	Difference in three samples (%)	Remarks
		mesh	wt (g)					
A	Effect of Zn surface area	20	1	0.1	2-5	0.051 ^c		{ incomplete conversion
		20	2	0.1	2-5	0.070	10	
		dust	1	0.1	2-3	0.303	2	
B	Variation in quantity of nickelic oxide	dust	1	0.1	3-5	0.303	1.3	7.1% decrease in activity/g NiO ₂
		dust	1	0.5	3-5	0.295	1.6	
		dust	1	1.0	3-5	0.282	2	
C	Variation in quantity of zinc	dust	0.1	0.1	3-4	0.83	3	3.3% decrease in activity/g Zn
		dust	0.5	0.1	2-4	1.20	2	
		dust	1.5	0.1	2-4	1.16	2	

^a All combustions were performed at $640 \pm 10^\circ$ for 3 h using 5-6 mg of carrier water per analysis. Evidence for choosing this temperature is shown in Table II.

^b *t*-Benzoic acid was used for Series A and B, whilst *t*-anthranilic acid was used for Series C.

^c This figure was the average value of ten samples varying from 0.028 to 0.059 V/min/mg.

 TABLE II
 EFFECT OF TEMPERATURE AND TIME OF COMBUSTION^a

Wt. of zinc	Wt. of NiO ₂ (g)	Sample size (mg)	Wt. of H ₂ O (mg)	Temp. ($\pm 10^\circ$)	Time (h)	Spec. act. (V/min/mg)	% Difference in duplicate	Remarks
0.5	0.1	2-3	5-6	640	0.5	0.86	3	Incomplete conversion
0.5	0.1	2-3	5-6	640	1	1.20	2	{ Complete conversion and no diffusion
0.5	0.1	2-4	5-6	640	3	1.20	2	
0.5	0.1	2-3	5-6	640	5	1.20	1.7	
0.5	0.1	2-3	5-6	640	16	1.20	1.8	
0.5	0.1	2-3	5-6	690	10	1.14	0.5	
0.5	0.1	2-3	5-6	730	11	1.14	1.5	0.4% diffusion/h

^a Data in this table are referred to as Series D in the text.

is a slight decrease in specific activity from 1.20 to 1.16 V/min/mg. The value of 1.20 V/min/mg is considered to be a reference figure as data in Table II indicate. The authenticity of this reference value is also confirmed by the activity balance obtained from distribution experiments with anthranilic acid and its brominated derivatives⁸. The observed difference in specific activity can probably be attributed to absorption of tritium on to the catalyst surface. Since this effect was small (3%) for a large increase in zinc dust (300%), this variable was not investigated in further detail and for subsequent analyses (Tables II and III) a catalyst ratio of 5 parts of zinc dust to 1 part of nickelic oxide was used.

From the results in Table II, Series D, it is clear that complete conversion was obtained when a sample of size 2-4 mg was combusted at $640 \pm 10^\circ$ for 1 h. These

conditions are ideal for general analysis; however, if the temperature is raised at 690° or above, diffusion of the tritium through the pyrex tubes begins to occur.

The results of experiments designed to examine the remaining variables in the analytical procedure, *e.g.* sample size and carrier water are reported in Table III. The data indicates that when 0.2 g of zinc dust and 0.04 g of nickelic oxide are used per mg of sample the technique is applicable to sample sizes of up to 8 mg and a better precision in duplicate is obtained. Provided that sufficient zinc dust is present, the method seems to be indifferent to the amount of water carrier used. If no carrier is used, the results are low and the same effect is observed if the ratio of water carrier to zinc is very large, as the last analysis in Table III shows. An interesting observation emerges from this series of analyses and this concerns samples which are analysed several days after combustion. Under these conditions, results are usually 3–4% low probably due to the slow absorption of tritium on to the walls of the reaction tube. This discrepancy can be eliminated if the tubes are reheated to 640° for 10 min before analysis.

TABLE III
EFFECT OF SAMPLE SIZE AND WATER CARRIER^a

Series	Purpose of investigation	Sample (mg)	Zinc (g)	Nickelic oxide (g)	H ₂ O (mg)	Specific activity (V/min/mg)
E	Variation in sample size	1.24 ₃	0.25	0.05	5–6	1.18
		2.84 ₁	0.57	0.11	5–6	1.20
		5.06 ₈	1.01	0.20	10–11	1.20
		7.92 ₈	1.59	0.32	15–16	1.20
F	Variation in water carrier	2.84 ₁	0.57	0.11	5–6	1.20
		2.40 ₉	0.48	0.096	10–11	1.19
		3.12 ₈	0.65	0.13	15–16	1.20
		2.19 ₄	0.44	0.09	20–21	1.18

^a All combustions were performed at 640 ± 10° for 1 h.

Suggested analytical method

From the results of this paper, the following conversion procedure is suggested for reproducibility of 0.5%. Zinc dust (0.2 g) and nickelic oxide (0.04 g) per mg of sample is added to the reaction tube with water carrier (5–10 mg), the tube evacuated, sealed and heated at 640 ± 10° for 1 h.

This method has proved satisfactory for the analysis of tritium in the following compounds: anthranilic acid, benzoic acid, cholesterol, 2,4,6-tribromoaniline, 3,5-dibromoanthranilic acid, 5-bromoanthranilic acid, myoinositol, phthalic acid, octanol and octyl phthalate. Details of the analytical data associated with these compounds will be published with each individual project as it is completed.

ACKNOWLEDGEMENTS

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grants towards the purchase of the tritium counter and tritium gas. One of us (S. W. Law) also wishes to acknowledge financial support from the N.S.W. State Cancer Council.

SUMMARY

The WILZBACH one-step method for tritium analysis has been re-investigated because of difficulty in obtaining satisfactory results with the available catalysts. The important factors governing the conversion of tritium from an organic compound to the gaseous phase have been studied. Such factors include the use of zinc dust instead of zinc mesh for the reduction step, temperature of combustion, and the effect of variation in catalyst weight and sample size on conversion efficiency.

RÉSUMÉ

Les auteurs ont effectué une étude au sujet de la méthode de WILZBACH pour l'analyse du tritium par comptage; ils ont examiné les différents facteurs intervenant dans la formation du tritium gazeux, à partir de composés organiques.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die WILZBACH'sche Methode zur Bestimmung von Tritium nach dem Zählverfahren unter besonderer Berücksichtigung der Faktoren, welche die Überführung organisch gebundenen Tritiums in gasförmiges Tritium beeinflussen (Reduktionsmittel, Verbrennungstemperatur, Katalysator).

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p-(3-HYDROXY-3-PHENYLTRIAZENO)-PHENYLTRIMETHYL-AMMONIUM CHLORIDE AS A NEW COLOUR REAGENT FOR CERTAIN METAL IONS

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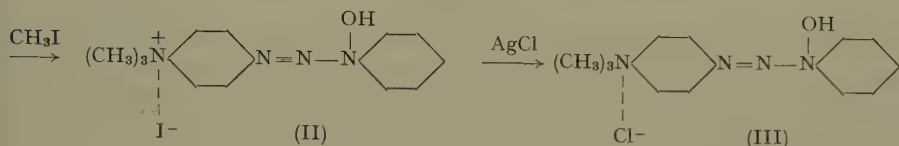
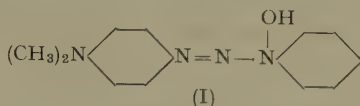
Water solubility is generally regarded as a desirable characteristic of organic reagents used in colorimetric analysis. In order to fulfil this condition, certain polar groups such as sulfonic acid, carboxylic acid or hydroxyl groups are introduced into the organic reagent in addition to the usual chelating groups. YOE¹, KLOOSTER², and EPHRAIM³ have studied the effect of introducing such solubilising groups and have shown that the introduction of such groups does not appreciably affect the properties of the complex-forming groups, but yields water-soluble inner complex anions rather than the usual insoluble inner complex precipitate with metal ions. In certain cases the selectivity and specificity of the reagent for certain metal ions is also increased by the introduction of such groups.

In organic chemistry, an excellent example of solubilisation is found in the case of high molecular ketonic compounds (steroids) which can be converted into water-soluble hydrazone derivatives with GIRARD reagent⁴. The presence of the highly polar quarternary ammonium group makes these compounds soluble and water extractable. In the present investigation an attempt has been made to prepare a new colorimetric reagent which is a derivative of the already known 3-hydroxy-1,3-diphenyltriazene proposed by SOGANI AND BHATTACHARYA⁵ as a reagent for palladium and other metal ions; these authors used the sulphonic acid derivative⁶ of the parent compound as a colorimetric reagent. However, the solubilising action of the trimethylammonium chloride group is greater than that of acidic groups, hence it could be expected that *p*-(3-hydroxy-3-phenyltriazeno)-phenyltrimethylammonium chloride would be more useful and also free from any interference which could be caused by the acidic groups in the analysis of cations. The present paper deals with the synthesis and qualitative reactions of the reagent. Spectrophotometric and quantitative studies of the reagent are still under investigation.

PREPARATION AND PROPERTIES OF THE REAGENT

The method used for the synthesis of the reagent was SOGANI AND BHATTACHARYA'S⁵ modification of BAMBERGER'S method⁷. Diazotised *p*-aminodimethylaniline was coupled with phenylhydroxylamine to give 1(*p*-dimethyl-amino-phenyl)-3 phenyl-3-hydroxy-triazene (I). This compound was converted to corresponding quarternary ammonium iodide (II) by mixing the dried product with excess of methyl iodide. After about 48 h, the precipitated quarternary ammonium iodide was filtered and

shaken with excess of freshly precipitated silver chloride suspension in water. The silver iodide precipitate and excess of silver chloride were filtered off and the required reagent (III) was obtained on evaporating the filtrate.



The composition of the product was checked by determining the nitrogen and the ionic chlorine contents. (Found: N = 18.01, Cl = 11.71. Calc. for $\text{C}_{15}\text{H}_{19}\text{N}_4\text{OCl}$: N = 18.27, Cl = 11.91). The reagent is yellowish green in colour; it shows no sharp m.p. but starts decomposing at about 180°.

REACTIONS WITH VARIOUS METAL IONS

Before the colorimetric determination of any metal ion was studied with the proposed reagent, qualitative tests were carried out by conventional procedures. A 1.0% solution of the reagent was prepared in distilled water and the reagent was added dropwise to about 0.5 ml of 1.0% salt solutions (usually chlorides) till the intensity of the colour was a maximum. The pH adjustments were made with *N* hydrochloric acid and 10% w/v sodium acetate, indicator paper or a pH meter being employed. The formation of the characteristic colour was observed both in the cold and on heating.

The colour reactions of the various metal ions with the reagent are summarised in Table I.

TABLE I

Metal ion	Optimum pH of the reaction	Colour of the complex	Sensitivity of the reaction (μg)	Remarks
Ni ⁺²	5.0-6.5	Bright yellow	0.08	Stable to heat up to 85°
Cu ⁺²	2.0-7.0	Chocolate brown	0.60	Stable to heat up to 80°
Co ⁺²	5.0-7.0	Dark brown	0.05	Stable to heat up to 80°
Mn ⁺²	5.5-7.0	Brown	—	Unstable to heat. N.Q.*
Cd ⁺² , Zn ⁺² , Pb ⁺²	Neutral	Light yellow	0.05	Unstable to heat. N.Q.*
Fe ⁺² , Fe ⁺³	3.0-4.5	Greenish blue	0.50	Unstable to heat. N.Q.*
V ⁺⁴	1.5-3.5	Light green	0.50	Unstable to heat. N.Q.*
Ti ⁺⁴	1.5-3.5	Orange	0.50	Unstable to heat. N.Q.*
Pd ⁺²	1.5-7.0	Yellowish brown	0.85	Stable to heat up to 90°
Hg ⁺²	4.0-7.0	Yellow	—	Unstable to heat
Ag ⁺	4.0-7.0	Yellow	—	Reduced to metallic state

* N.Q. = not quantitative

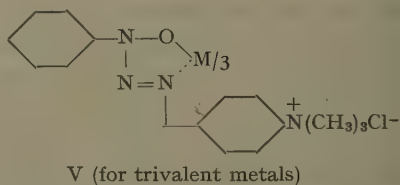
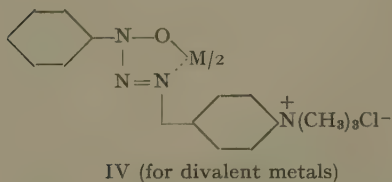
In the case of silver and lead, the ionic chloride of the reagent first precipitated the respective halides. With an excess of lead, the salt formed a yellow colour while silver was reduced to metallic state.

EFFECT OF NEUTRAL SALTS AND INTERFERING ACID RADICALS

In most cases the colour of the complex was not affected by the presence of indifferent metal ions (chlorides, sulphates and nitrates of alkali and alkaline earth metals) up to a concentration of 10 to 15%. The acid radicals also have no appreciable effect because the complex formation takes place in acidic medium, but the reactions are masked completely by the presence of cyanide ions.

DISCUSSION

The quarternary ammonium group can be used satisfactorily to solubilise organic reagents and their metal complexes. The introduction of this group into the molecule of 3-hydroxy-1,3-diphenyltriazene does not affect the complex-forming properties of the group $-N=N-N-OH$. The metal complexes of the reagent in solution may be represented by the following general formulae



in which the presence of a polar group prevents the precipitation of the complex.

The introduction of the salt-like group does not interfere with the reactions of the metal ions. The ionisation of the trimethylammonium chloride group is much greater than that of the usual acidic groups such as the sulphonic acid group and the solubilities of the reagent and its metal complexes are therefore also larger. The reagent satisfies the requirements of an ideal colorimetric and complexometric reagent.

SUMMARY

The synthesis and qualitative reactions of *p*-(3-hydroxy-3-phenyltriazeno)phenyltrimethylammonium chloride are described. The solubilising effect of the quarternary ammonium group is studied; this group is valuable for the conversion of organic precipitants to colorimetric reagents.

RÉSUMÉ

Le chlorure de *p*-(hydroxy-3-phényltriazéno-3)-phényltriméthylammonium est proposé comme nouveau réactif coloré pour certains cations. L'effet solubilisant du groupe ammonium quaternaire a été examiné.

ZUSAMMENFASSUNG

Als neues Farbreagenz für eine Anzahl Metallionen wird das *p*-(3-Hydroxy-3-phenyltriazeno)-phenyltrimethylammoniumchlorid empfohlen.

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THE DETERMINATION OF FLUORIDES IN NATURAL WATERS,
WITH PARTICULAR REFERENCE TO SEA WATER

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Until recently methods for the determination of traces of fluoride in natural waters were almost all based on the ability of the ion to destroy the coloured organic complexes of certain metals, *viz.* zirconium, thorium, titanium, aluminium or ferric iron, through the formation of the very stable complex fluorides of the metals. The decrease in colour of the metal complex is a measure of the fluoride concentration. Beer's law is frequently not obeyed in these procedures owing to the diversity of complex fluorides which can co-exist in the solution.

These methods suffer from the disadvantage that sulphate ion also bleaches the organic complexes owing to the formation of stable complex sulphates, *e.g.* $[\text{ZrO}(\text{SO}_4)_2]^{-2}$. The interference of sulphate can be reduced in a number of ways. The reaction may be carried out^{1,2} in the presence of a great excess of sulphuric acid, which produces a more stable reagent³, but with a considerable loss in sensitivity. The effect may be compensated^{4,5} for by raising the sulphate content of the sample to a constant level by the addition of sodium sulphate. Precipitation of the sulphate with barium ions⁶ introduces inaccuracies owing to co-precipitation effects and is tedious. Fluoride can be separated⁷ from sulphate in brackish waters by passing the sample through the barium form of a cation exchange resin (Zeocarb 215), but large concentrations of chloride interfere. In a method⁸ for the determination of fluoride in drinking water by the zirconium-eriochrome cyanine R complex, the interference of sulphate has been eliminated by a preliminary separation of the fluoride by adsorption on an anion exchange resin. Steam distillation^{9,10} of fluoride from perchloric, sulphuric or phosphoric acid¹¹ medium in the presence of silica, serves to separate the ion from sulphate and most other interfering ions. The process is rather time consuming and requires close control, poor recoveries being obtained at low fluoride levels, particularly in the presence of aluminium.

The high concentration of chloride found in sea and ocean water has a considerable influence on the bleaching action of fluoride on the lake, and tends to cause the latter to precipitate. Since the $\text{SO}_4^{-2} : \text{F}^-$ ratio of sea water is very high (1500:1) the interference of sulphate is likely to be particularly severe in this medium. For the determination of fluoride in sea water the bleaching of the reddish-violet lake formed between zirconyl ion and alizarin red S has been used¹². The method is not particularly sensitive, is slow and of poor precision. In order to control sulphate interference ANSELM AND ROBINSON² have determined fluoride in sea water using this lake in a

sulphuric acid medium. This reduces the sensitivity even further and the reaction requires 6 h to attain equilibrium. MATIDA¹³ has applied this procedure to the determination of fluoride in the surface and shallow waters of Tokyo Bay.

Recently, a new spot test for the detection of fluoride ion has been reported¹⁴ and the reaction has been applied¹⁵ to the determination of fluorine in organic compounds. In this test, the fluoride ion reacts with the red cerous chelate of alizarin complexone (1:2-dihydroxy-anthraquinonyl-3-methylamine-N:N-diacetic acid); the resultant blue complex apparently contains fluoride and cerium alizarin complexone in a 1:1 molar ratio¹⁶. The reagent of BELCHER *et al.*^{14,15} has been applied¹⁷ to the determination of fluoride in deposit gauge samples, after a preliminary separation of interfering cations by ion exchange.

In these laboratories an investigation of the constancy of ionic composition of sea and ocean waters is in progress. It was, therefore, decided to investigate the potentialities of this reagent for the determination of fluoride in sea water.

Development of the method

By simple preliminary tests the sensitivity¹⁸ of the reagent to fluoride was found to be *ca.* 0.004 $\mu\text{g}/\text{cm}^2$.

It has been found¹⁶ that complexes with alizarin complexone are formed by scandium and yttrium and all the lanthanons, and of these only those of lanthanum, cerium, praseodymium, and to a lesser extent samarium, form a fluoride complex. While investigating the possibility of achieving a higher sensitivity by use of other lanthanon elements the above observations were confirmed independently. Thus it was found that lanthanum, cerium, praseodymium, neodymium and samarium formed the fluoride complex (the sensitivity to fluoride falling with increasing atomic number) and terbium, erbium, ytterbium, scandium and yttrium failed to do so. The intermediate elements europium and gadolinium form extremely weakly coloured fluoride complexes. Elements Nos. 61, 66, 67, 69 and 71 were not examined. The wavelengths of the absorption maxima of the various lanthanon-alizarin complexones were not significantly different, neither was there any wavelength shift among the

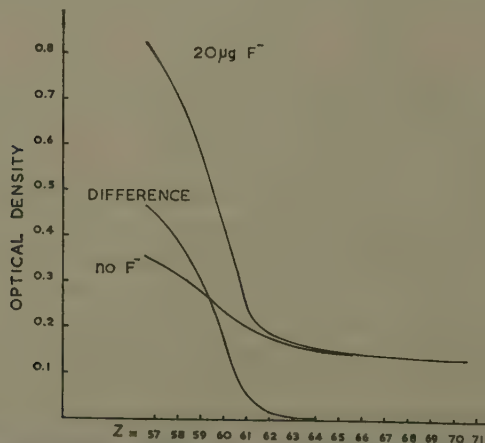


Fig. 1. Optical densities of the fluoride complexes of the chelates of the lanthanons with alizarin complexone as a function of atomic number.

fluoride complexes of the elements from lanthanum to samarium. The results, which are shown in Fig. 1, were obtained by adding 2.0-ml volumes of 0.002 *M* alizarin complexone and 0.004 *M* lanthanon solutions to 20 μg of fluoride in 25-ml graduated flasks containing acetic acid/sodium acetate buffer and 4 ml of acetone (acetone enhances the colour of the fluoride complex; *vide infra*). Twenty minutes after diluting to volume the optical densities of the solutions were measured at 622 $m\mu$ in 1-cm cells against a reagent blank. Owing to the greater sensitivity to fluoride shown by lanthanum (Fig. 1) it was decided to use this element in the development of the method.

Absorption spectra

The absorption spectra of the lanthanum-alizarin complexone chelate and its complex with fluoride are shown in Fig. 2. The maximum sensitivity to fluoride is at 622 $m\mu$.

Effect of variation of lanthanum concentration

In a preliminary investigation of the influence of lanthanum concentration upon the fluoride sensitivity and blank, it was found that as its concentration in the final volume was increased above *ca.* 0.0004 *M*, precipitation of the complex occurred. This effect was overcome by stabilising the complex with acetone, sufficient acetone being added to the solutions before addition of the reagents, to make its final concentration not less than 12% vol/vol with respect to acetone. In addition to having a stabilising effect, the presence of acetone increased the sensitivity of the reagent to fluoride by *ca.* 60% (to 0.0018 $\mu\text{g}/\text{cm}^2$). The effect of variation of lanthanum concentration in the presence of acetone is shown in Table I. The results were obtained by making additions of 0.004 *M* lanthanum solution to a 25-ml graduated flask containing 25 μg of fluoride, 2.5 ml *M* sodium acetate solution, 2.5 ml *N* acetic acid solution, 4.0 ml acetone and 2.0 ml 0.002 *M* alizarin complexone. They show that the final concentration of lanthanum in the developed solution should be about 0.0003 *M*.

TABLE I

EFFECT OF VARIATION OF LANTHANUM CONCENTRATION UPON OPTICAL DENSITY OF SOLUTIONS

ml 0.004 <i>M</i> La	O.D. at 622 $m\mu$ ^a		Difference
	Blank	25 μg F ⁻	
0.0	0.028	0.028	—
1.0	0.256	0.763	0.507
1.5	0.296	0.870	0.574
2.0	0.314	0.895	0.581
3.0	0.337	0.905	0.568
4.0	0.348	0.900	0.552

^a Measured in 1-cm cells

Conformity to Beer's law

Fig. 3 shows the linear relationship, up to *ca.* 25 μg , between the fluoride content and the optical density, and also illustrates the influence of reagent concentration upon the linearity. Curve A was obtained by use of equal volumes (2.0 ml) of 0.002 *M*

and 0.004 *M* alizarin complexone and lanthanum respectively, when the relationship is linear up to 20 μg of fluoride. A 25% increase in the concentration of both reagents produces (curve B) an extension of the linearity to *ca.* 25 μg .

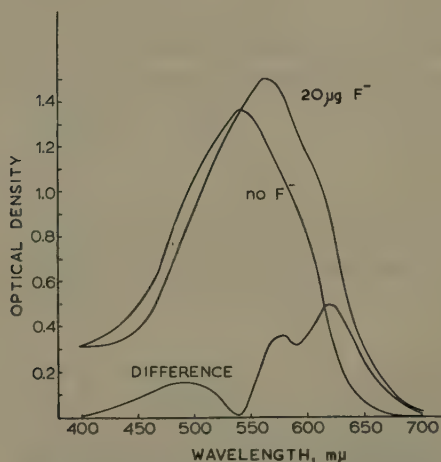


Fig. 2. Absorption curves of the lanthanum-alizarin complexone chelate and its fluoride complex. 1-cm cell; 25-ml volume.

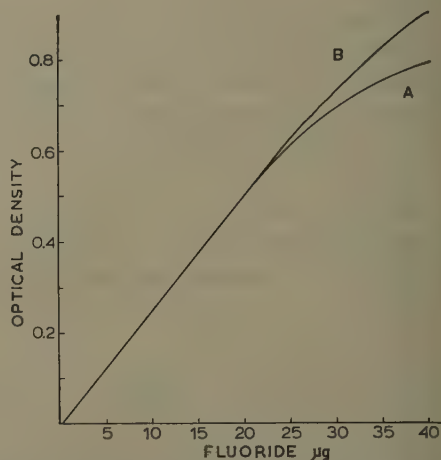


Fig. 3. Calibration curve for fluoride using the lanthanum-alizarin complexone reagent. 1-cm cell, 25-ml volume, 622 $m\mu$. Curve A: 2.0 ml 0.002 *M* alizarin complexone, 2.0 ml 0.004 *M* lanthanum. Curve B: 2.5 ml 0.002 *M* alizarin complexone, 2.5 ml 0.004 *M* lanthanum.

Stability of developed coloured complexes

In non-saline solutions, the colour development of the lanthanum-alizarin complexone and of its fluoride complex was found to be practically instantaneous, and both complexes were remarkably stable, showing little change even after several days. The presence of 15 ml of artificial sea water (prepared as described by LYMAN AND FLEMING¹⁹ from fluoride-free reagents) delayed the development of the maximum colour slightly, but had no effect on its stability.

It was found that the aqueous solutions of alizarin complexone aged, resulting in a decrease in sensitivity to fluoride, thus, the optical density calibration value for 25 μg of fluoride dropped from 0.585 to 0.528 in a week. Since the colour of the developed reagent blank was known to be exceptionally stable it was decided to prepare a combined reagent containing lanthanum-alizarin complexone, acetone and the buffering components. With this reagent the optical density calibration for 25 μg of fluoride did not change appreciably in a week.

Effect of pH variation

Aliquots (8.0 ml) of the combined reagent, described below but containing no acetic acid, were added to 25-ml graduated flasks containing 15-ml aliquots of artificial sea water and varying amounts of 6 *M* acetic acid solution. The optical densities were measured and compared with those of identical solutions containing 20 μg of fluoride. The results shown in Table II indicate that the pH of the solution must be kept within the range 4.45-4.85. Owing to the high acetone content of the solution the pH values

shown in Table II must be considered to be only apparent values. It was found that the pH of the buffered solution was slightly lowered by the presence of salts. In order to make the pH values of saline and non-saline solutions the same, a standard amount of dilute acetic acid solution must be added to the reagent blank.

TABLE II

EFFECT OF APPARENT pH UPON THE OPTICAL DENSITIES OF LANTHANUM-ALIZARIN COMPLEXONE AND ITS FLUORIDE COMPLEX

ml 6 M acetic acid	apparent pH	Optical density ^a		Difference
		Artificial sea water	Artificial sea water + 20 µg F ⁻	
0	6.20	0.471	0.566	0.095
0.25	5.08	0.423	0.841	0.418
0.30	5.02	0.421	0.850	0.429
0.50	4.84	0.409	0.856	0.447
0.60	4.76	0.404	0.853	0.449
0.70	4.69	0.394	0.842	0.448
0.90	4.57	0.380	0.828	0.448
1.00	4.43	0.376	0.820	0.444
1.25	4.32	0.354	0.791	0.437
1.50	4.25	0.340	0.757	0.417
2.00	4.15	0.308	0.704	0.396
2.50	4.04	0.275	0.651	0.376
3.00	3.97	0.248	0.600	0.352
4.00	3.82	0.174	0.461	0.287
6.00	3.71	0.122	0.322	0.200

^a Optical densities measured at 622 mµ in 1-cm cells, against distilled water

Method

Unless otherwise stated, a Unicam S.P. 500 spectrophotometer was employed for all optical density measurements. A slit width of *ca.* 0.05 mm was used. pH measurements were made with a Pye Master pH meter using a glass electrode.

Reagents

(1) Combined lanthanum-alizarin complexone reagent. Dissolve 0.0479 g of alizarin complexone in 0.1 ml of concentrated ammonium hydroxide and 1.0 ml of 20% w/v ammonium acetate, together with a few ml of distilled water. Filter the solution through a small Whatman No. 1 paper into a 200-ml graduated flask containing 8.2 g of anhydrous sodium acetate (A.R.), 6.0 ml of glacial acetic acid and sufficient distilled water to dissolve the solids. Wash the filter paper with a small volume of water. Add 100 ml of acetone slowly, with swirling. Dissolve 0.0408 g of lanthanum oxide (spectrographic grade) in 2.5 ml of 2 M hydrochloric acid, warming gently to aid dissolution, and mix with the aqueous acetone solution. Dilute to 200 ml with water. Mix well and readjust the volume after about 30 min. The reagent is stable for at least one week.

(2) Sodium fluoride solution. Prepare a stock solution containing 1 mg of fluoride/ml by dissolving 2.210 g of sodium fluoride in 50 ml of water containing 1 ml of 0.1 N sodium hydroxide and diluting to 1 l. Dilute the stock solution daily to give a working standard containing 10 µg of fluoride/ml.

Procedure

To 15 ml of filtered (Whatman No. 1 paper) sea water, contained in a 25-ml graduated flask, add 8.0 ml of the combined reagent, dilute to volume and mix well. With samples having chlorinities considerably less than 20‰ it is necessary to add also $(0.4-0.02 x)$ ml of 6 *N* acetic acid, where x is the chlorinity of the water. The

TABLE III
INTERFERENCE OF ANIONS ON THE DETERMINATION OF FLUORIDE

<i>Anion</i>	<i>Added as</i>	<i>Amount of anion added</i>	<i>Optical Density^a</i>
None	—	—	0.497
Borate	H ₃ BO ₃	0.25 mg	0.497
Borate	H ₃ BO ₃	0.50 mg	0.497
Bromide	KBr	0.75 mg	0.498
Bromide	KBr	1.25 mg	0.501
Chloride	NaCl	0.085 g	0.513
Chloride	NaCl	0.170 g	0.513
Chloride	NaCl	0.255 g	0.524
Chloride	NaCl	0.340 g	0.532
EDTA	disodium salt	1 ml 0.001 <i>M</i>	0.444
Iodide	KI	2 µg	0.497
Perchlorate	KClO ₄	2 mg	0.497
Phosphate	KH ₂ PO ₄	1 µg	0.496
Phosphate	KH ₂ PO ₄	10 µg	0.494
Silicate	Na ₂ SiO ₃	26 µg	0.495
Silicate	Na ₂ SiO ₃	65 µg	0.498
Silicate	Na ₂ SiO ₃	5.1 mg	0.494
Silicate	Na ₂ SiO ₃	16.5 mg	0.484
Sulphate	Na ₂ SO ₄	26.4 mg	0.492
Sulphate	Na ₂ SO ₄	52.8 mg	0.482
Nitrate	KNO ₃	10 µg	0.495
Nitrite	NaNO ₂	10 µg	0.496

^a Measured at 622 *mμ* in 1-cm cells against a reagent blank

chlorinity need only be known to the nearest 5 units. A reagent blank is similarly prepared by adding the same volume of the reagent to 15 ml of distilled water containing 0.4 ml of the dilute acetic acid solution.

The blank and sample solutions, when diluted to volume, should have apparent pH values of 4.50 ± 0.02 . Measure the optical density of the sample solution at 622 *mμ* in a 1-cm cell against the reagent blank after 30 min. Calibrate the method in the same manner using 15-ml aliquots of distilled water containing 1.0, 1.5 and 2 ml of the dilute standard fluoride solution with the addition of 0.4 ml of 6 *N* acetic acid. For sea waters having chlorinities in the range 15 to 20‰ the observed optical densities of the samples must be multiplied by 1.040 to compensate for salt error. Correction factors at other chlorinities may be interpolated from the data in Table V.

Effect of other anions and cations

The effect of various anions and cations on the determination of 20 µg of fluoride,

by the method described above, was investigated. The optical densities measured against a reagent blank, are shown in Tables III and IV respectively. The optical density difference for 20 μg of fluoride is 0.497.

In these tables the amounts of the various cations or anions under investigation were chosen generally with reference to ocean waters, in which the concentrations of chloride, sulphate, bromide, borate, magnesium and calcium are relatively high. The more reliable estimations of the amount of aluminium in ocean waters indicate that the element is present to the extent of only about 0.01 p.p.m.; at this concentration its interference in the method is negligible. No interference would be antici-

TABLE IV
INTERFERENCE OF CATIONS IN THE DETERMINATION OF FLUORIDE

<i>Cation</i>	<i>Added as</i>	<i>Amount of cation added</i>	<i>Optical density^a</i>
None	—	—	0.497
Aluminium	Al NH ₄ (SO ₄) ₂ · 12 H ₂ O	0.5 μg	0.492
Aluminium	Al NH ₄ (SO ₄) ₂ · 12 H ₂ O	1.0 μg	0.479
Aluminium	Al NH ₄ (SO ₄) ₂ · 12 H ₂ O	2.0 μg	0.475
Aluminium	Al NH ₄ (SO ₄) ₂ · 12 H ₂ O	8.0 μg	0.415
Barium	BaCl ₂ · 2 H ₂ O	2.0 μg	0.496
Calcium	Ca(ClO ₄) ₂	4.2 mg	0.494
Calcium	Ca(ClO ₄) ₂	8.4 mg	0.492
Cobalt	CoCl ₂ · 6 H ₂ O	10.0 μg	0.525
Copper	CuSO ₄ · 5 H ₂ O	10.0 μg	0.514
Iron	NH ₄ Fe(SO ₄) ₂ · 12 H ₂ O	1.0 μg	0.499
Iron	NH ₄ Fe(SO ₄) ₂ · 12 H ₂ O	50.0 μg	0.478
Magnesium	Mg(ClO ₄) ₂	12.7 mg	0.455
Magnesium	Mg(ClO ₄) ₂	25.4 mg	0.422
Nickel	Ni(NO ₃) ₂ · 6 H ₂ O	10.0 μg	0.520
Uranium	UO ₂ (NO ₃) ₂ · 6 H ₂ O	100.0 μg	0.497
Uranium	UO ₂ (NO ₃) ₂ · 6 H ₂ O	1.0 mg	0.506
Zinc	ZnSO ₄ · 7 H ₂ O	10.0 μg	0.500

^a Measured at 622 $m\mu$ in 1-cm cells against a reagent blank

ated from iron, copper, nickel, cobalt and zinc since their concentrations in sea waters are below 0.1 p.p.m.

Application of the method to sea water

The effect of the salts present in sea water upon the sensitivity of the method to fluoride was determined. Known amounts of fluoride were added to 15-ml aliquots of distilled water and artificial sea waters having chlorinities of 5.05, 10.13, 15.20 and 20.26‰. These solutions were treated with 8 ml of the mixed reagent and appropriate volumes of 6 *N* acetic acid to give the solution a pH of 4.50 ± 0.02 , when made up to a volume of 25 ml. Optical densities (O.D.) measured against the reagent blanks are shown in Table V.

At each chlorinity, Beer's law is followed closely up to 25 μg of fluoride. Since the average optical density increments of fluoride are identical at chlorinities 15 and

20‰, the salt error correction for sea water samples having chlorinities in this range is a constant and equal to +4.0%. From the data in Table IV it appears that most of the salt error is due to magnesium.

Reproducibility of the method

Replicate analyses (11) were performed, according to the method, on 15-ml portions of a filtered surface sample (46°30' N, 8°00' W) and gave a mean fluoride content of 1.371 µg/ml. The standard deviation was 0.0038 µg/ml and the coefficient of variation

TABLE V
THE EFFECT OF SALTS UPON THE FLUORIDE DETERMINATION

Fluoride added (µg)	Chlorinity of sea water (Cl ‰)									
	0		5.05		10.13		15.20		20.26	
	O.D. ^a	O.D./µgF ⁻	O.D. ^a	O.D./µgF ⁻	O.D. ^a	O.D./µgF ⁻	O.D. ^a	O.D./µgF ⁻	O.D. ^a	O.D./µgF ⁻
15	0.376	0.0251	0.372	0.0248	0.368	0.0246	0.365	0.0243	0.364	0.0243
18	0.447	0.0248	0.444	0.0247	0.437	0.0243	0.432	0.0240	0.432	0.0240
20	0.495	0.0247	0.487	0.0244	0.479	0.0240	0.476	0.0238	0.475	0.0238
22.5	0.556	0.0247	0.548	0.0244	0.539	0.0240	0.533	0.0237	0.533	0.0237
25.0	0.617	0.0247	0.607	0.0243	0.598	0.0239	0.591	0.0236	0.590	0.0236
Average O.D./µg	—	0.0248	—	0.0245	—	0.0241	—	0.0238	—	0.0238
Average salt error	0		-1.2%		-2.9%		-4.0%		-4.0%	

* Optical densities measured at 622 mµ in 1-cm cells against a reagent blank

0.28%. The results were obtained by measuring the optical densities, against a reagent blank, with an Optika CF4 spectrophotometer.

In order to check the recovery of fluoride from sea water the optical density developed with known amounts of fluoride added to 12.5-ml aliquots of the same sea water were measured, and the fluoride recovery was evaluated from calibration curves

TABLE VI
RECOVERIES OF ADDED FLUORIDE FROM A SEA WATER

µg F ⁻ added	Optical density ^a Difference	Fluoride (µg) from calibration curve	Fluoride (µg) recovery
0	0.418 0.419	17.40	—
4.00	0.507 0.507 0.506	21.35 21.35 21.30	3.95 3.95 3.90
5.00	0.531 0.531 0.531	22.40 22.40 22.40	5.00 5.00 5.00
6.00	0.556 0.557 0.554	23.50 23.50 23.40	6.10 6.10 6.00

* Measured at 622 mµ against the reagent blank in 1-cm cells

derived from Table V. The results which are given in Table VI show that the recovery is quantitative and that the average error is $\pm 0.05 \mu\text{g}$ with *ca.* 20 μg of fluoride.

Application of the method to non-saline waters

The method described for sea waters can be applied directly to the majority of fresh waters without the necessity of applying the salt error correction, since the concentrations in such waters of chloride, sulphate, magnesium and other ions contributing to the salt effect, are negligible.

The most serious interference with the reagent is that of aluminium, which, although it does not react with the alizarin complexone to any appreciable extent, except at high concentrations, forms extremely stable fluoro compounds, particularly AlF_6^{-3} , and thereby prevents the reaction of fluoride with the lanthanum-alizarin complexone complex. The effectiveness of any procedure designed to separate aluminium from fluoride, or *vice versa*, is obviously dependent upon the relative molar concentrations of these ions in the solution. An attempt¹⁷ to remove the aluminium from solution, prior to the fluoride determination, by use of a cation exchange resin was not entirely successful, the aluminium-fluoro complexes proving too stable to be broken down by the resin. Incomplete recoveries of micro amounts of fluoride have also been observed⁷ when using a strongly basic anion exchange resin as a means of separation from similar concentrations of aluminium. The classical method of sep-

TABLE VII

SEPARATION OF ALUMINIUM FROM FLUORIDE BY CONTINUOUS SOLVENT EXTRACTION AS OXINATE

Sample content	Optical density ^a	$\mu\text{g F}^-$ recovered
2 $\mu\text{g F}^-$ standard	0.294	12.0
2 $\mu\text{g F}^-$ extracted	0.293	12.0
2 $\mu\text{g F}^-$ + 12 $\mu\text{g Al}^{+3}$ extracted	0.299	12.3
-do-	0.294	12.0
2 $\mu\text{g F}^-$ + 12 $\mu\text{g Al}^{+3}$ without extraction	0.210	8.6
2 $\mu\text{g F}^-$ + 120 $\mu\text{g Al}^{+3}$ extracted ^b	0.285	11.7
-do-	0.281	11.5
-do-	0.284	11.6
2 $\mu\text{g F}^-$ + 120.0 $\mu\text{g Al}^{+3}$ without extraction	Less than reagent blank	0.0

Optical densities measured against a reagent blank

5.0 ml acetone/oxine used in the extraction, followed by a further 5.0 ml after 20 min

ration of fluoride by distillation as a mixture of silicon tetrafluoride and hydrofluoric acid from acid solution is also unsatisfactory in the presence of much aluminium, and the effectiveness of phosphoric acid in the prevention of aluminium interference in this distillation has recently²⁰ been questioned.

For solutions which contain 2 p.p.m. of aluminium and fluoride the authors have found that complete removal of aluminium as oxinate can be achieved by use of a continuous solvent extraction apparatus²¹. To 20.0 ml of the sample solution in the extractor was added 2.0 ml of 2 *M* sodium acetate solution, 0.45 ml of 6.0 *N* acetic acid solution, and, with mixing, 1.0 ml of a 20% solution of 8-hydroxyquinoline in acetone. After the extraction was completed the aqueous phase was separated from the chloroform contained in the extractor, and filtered through a small filter paper

which was washed with water. The combined filtrate and washings were diluted to 50 ml. Water containing 2 p.p.m. of fluoride was treated in the same manner. Aliquots (20 ml) were used for the fluoride determination in each case. The results, together with those obtained at higher aluminium concentrations, are given in Table VII, and show that by this extraction procedure fluoride can be determined in the presence of a forty-fold stoichiometric excess of aluminium. For comparison the optical density differences of the solution without extraction are included in the table. In addition, this extraction procedure will remove many other possible interfering cations, e.g. iron(III).

SUMMARY

The chelate formed between lanthanum and alizarin complexone has been used as the basis of a method for the determination of fluoride in natural waters, with special reference to sea water. The fluoride complex formed with the reagent is developed rapidly at pH 4.50 by the addition of a single buffered reagent and is stable for several days. The fluoride complex is formed in 16% v/v acetone solution; the acetone stabilises the reagent and increases its sensitivity to 0.0018 $\mu\text{g}/\text{cm}^2$. Beer's law is followed up to ca. 25 μg of fluoride. The interference of inorganic ions present in natural waters has been investigated. Abnormally large amounts of aluminium interfere seriously, but can be removed by extraction as its oxinate in a continuous extractor. For sea water of chlorinity within the range 15 to 20‰ the salt error correction is constant and equal to 4.0%. The method showed a coefficient of variation of 0.3% with a sea water containing 1.37 μg of fluoride/ml.

RÉSUMÉ

Une nouvelle méthode a été mise au point pour le dosage spectrophotochimique des fluorures dans les eaux, en particulier, dans l'eau de mer. Elle est basée sur la réaction obtenue avec le réactif lanthane-"alizarin complexone" (acide dihydroxy-1,2-anthraquinonyl-3-méthylamine-N,N-diacétique).

ZUSAMMENFASSUNG

Beschreibung einer neuen Methode zur Bestimmung von Fluorid in Wasser, besonders Meerwasser. Sie beruht auf der Messung der optischen Dichte des Komplexes, der mit Lanthan-Alizarin-komplexon entsteht.

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DETERMINATION OF SILICA IN IRON ORE

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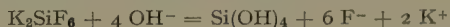
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(Received January 10th, 1961)

The percentage of silica in iron ore is usually determined in the course of a more or less complete analysis, following alkaline fusion. In many instances, the emphasis is on silica alone, and one may prefer a method that gives only the silica content.

We have modified previously known methods for the determination of silica as the sparingly soluble potassium fluosilicate, and have developed a useful titrimetric method for silica in iron ore. The advantages over previously used methods are speed and applicability over the whole range 0.5–20% of silica.

LANGMYHR¹ has shown that silica, hydrofluoric acid and water form a constant-boiling system with the composition 10% hydrofluoric acid, 36% fluosilicic acid and 54% water and with a boiling point of 116° at 1 atm. Below the corresponding concentration of total silica and below this boiling point, there is no loss of silicon on heating; this has been utilized in the procedure described below, where the ore sample is dissolved in a hot mixture of hydrochloric and hydrofluoric acid. The acid mixture also contains potassium chloride, and potassium fluosilicate is formed as the sample dissolves. After cooling, the precipitate is collected on a filter and determined titrimetrically according to the net reaction



Determination of silica in iron and carbon steel as potassium fluosilicate has been described by KORDON² and the method has been extended to alloyed steel by VANDAELEND JEHENSON³. SAJO⁴ has described a similar method for ores, slags and ceramics. LANGMYHR's principle of dissolving the sample in a hot mixture of hydrochloric and hydrofluoric acids was not employed by these workers, who all added potassium chloride and hydrofluoric acid to the already dissolved sample.

Our results indicate that calcium interferes in the presence of trivalent iron; SAJO neglects this complication.

The precipitate of potassium fluosilicate may be washed with an ethanolic solution of potassium chloride, as described by SAJO⁴ and by MARIMOTO AND MIZUNO⁵, but in our opinion an aqueous solution may be used with certain advantage, if the procedure is adjusted accordingly.

EXPERIMENTAL

Procedure

From a sample of finely ground ore, 0.1–0.4 g is weighed into a 200-ml polytrifluoroethylene beaker. After addition of 15 ml of concentrated hydrochloric acid, 10 ml of 10% hydrofluoric acid and 5 ml of 20% potassium chloride solution, the beaker is

placed on a boiling water-bath for 1 h. After 30 min, the ferric iron is reduced by addition of saturated aqueous stannous chloride solution; 1 ml usually suffices. After complete reaction, the solution is diluted with 15 ml of distilled water and the beaker is cooled for about 15 min in cold water.

The precipitate formed is collected on a cellulose filter pad, placed on a polyethylene sieve disc in a polyethylene funnel. The filtrate is collected in a plastic beaker. The precipitate is washed with cold 20% potassium chloride, in 3-ml portions, until *ca.* 20 ml of collected filtrate changes from red to yellow with 2 drops of 0.1 *N* sodium hydroxide and methyl red as indicator. The filter pad with the precipitate is transferred quantitatively to a 400-ml plastic beaker, suspended in *ca.* 100 ml of boiling water and is titrated with 0.1 *N* sodium hydroxide with phenolphthalein as indicator.

DISCUSSION

If the precipitate is washed with a 5% potassium chloride solution in 50% aqueous ethanol, practically none of the potassium fluosilicate dissolves, and the percentage of silica can be calculated according to theory.

$$\% \text{SiO}_2 = 0.150 \cdot \text{ml NaOH/g sample}$$

We have found that the procedure recommended here gives reproducible results, but 8.5% of the precipitate dissolves in the wash fluid, and the factor 0.150 must be changed to the empirical factor 0.160, which also corresponds to the blanks in our reagents. Washing with an aqueous solution of potassium salts is also described by KORDON² and has the advantage of greater speed over an ethanolic solution. An

TABLE I

Sample	% SiO ₂ grav.	% SiO ₂ Volumetric not reduced	% SiO ₂ Volumetric reduced	% CaO
Kip-D ⁵ <i>ca.</i> 60% Fe	3.18	3.52	3.15	6.7
Kip-D ⁵ <i>ca.</i> 60% Fe	4.23	4.42	4.21	7.5

TABLE II

Sample	% SiO ₂ grav.	% SiO ₂ volumetric	% deviation abs.	Spread in parallel runs
Mesabi standard	2.08	2.05 2.06	—0.025	0.01
Luossavaara Cl	3.96	3.96 3.94	—0.01	0.02
Kiruna B	2.21	2.17 2.18	—0.035	0.01
Tuolluvaara A	3.20	3.28 3.20	+0.04	0.08
Tuolluvaara Cl	3.58	3.56 3.54	—0.03	0.02

empirically calibrated method is usually inevitable in routine work, and a simple nomogram can be recommended. The digestion time in the first reaction must not be cut below 60 min, as we have found that the precipitate remains too soluble with shorter reaction times.

TABLE III

Sample	Luossavaara D ²	Kiruna D ³	Nimba	
% known	SiO ₂	9.30	2.69	3.52
	Fe ₂ O ₃	1.9	3.0	93.8
	Fe ₃ O ₄	78.2	80.9	—
	MnO	0.1	0.1	0.1
	CaO	2.7	5.3	0.3
	MgO	1.3	0.9	1.5
	Al ₂ O ₃	1.6	0.5	1.1
	TiO ₂	0.7	0.2	0.2
	V ₂ O ₅	0.2	0.2	—
	P ₂ O ₅	0.8	4.3	0.2
	S	0.03	0.02	0.03
	CO ₂	1.2	0.4	—
	Na ₂ O	0.5	0.1	—
	K ₂ O	0.5	0.3	—
	CuO	0.02	0.04	—
SiO ₂ % found	60 min	9.34	2.82	3.51
	diges-	9.25	2.88	3.50
	tion	9.25	2.72	3.48
	90 min	9.43	3.04	3.64
	diges-	9.75	3.20	3.58
	tion	9.38	3.10	3.59

TABLE IV

INFLUENCE OF ALUMINIUM AND TITANIUM

Added mg SiO ₂	Added mg Al ⁺⁺³	Added mg Ti ⁺⁺⁴	Found mg SiO ₂	Rel. deviation	
16.45	5.0		16.60	+0.9	60 min digestion
13.60	10.0		13.70	+0.7	
14.15	15.0		14.65	+3.5	
14.10		5.0	14.05	-0.4	
13.62		10.0	13.70	+0.6	
14.60		15.0	15.20	+4.1	
11.05	5.0		11.10	+0.5	90 min digestion
11.90	10.0		13.80	+17.5	
15.95	15.0		19.08	+19.8	
12.30		5.0	12.30	± 0	
15.40		10.0	16.00	+3.9	
13.10		15.0	13.95	+6.5	

The recommended time on the water-bath — 60 min — was also found to be optimal with regard to interferences from other constituents of the ore, especially calcium, aluminium and titanium, which may coprecipitate if too much of the original hydrochloric acid evaporates. The presence of these elements also necessitated the use of hydrochloric acid in the dissolution of the ore; otherwise a combination of hydrofluoric acid and potassium chloride was found to convert the silica to potassium silicate.

The Lappland iron ores contain calcium as apatite, and the combination of trivalent iron and calcium interferes with the determination of silica, unless the iron is reduced, as is shown in Table I.

The method was developed for Kiruna ore, but it was tested on other ores with good results (Table II).

The influence of digestion time is shown in Tables III and IV. In Table III, natural ore samples were used; in Table IV, large amounts of interfering elements were added in synthetic samples. The iron is not reduced to the divalent state.

Aluminium and titanium were found in the final solution after titration. The interference of these two elements through coprecipitation is the most serious limitation of the method. In the filtrate after collection of the potassium fluosilicate, all the iron and phosphorus and probably other minor constituents are available for determination.

CONCLUSION

The method proposed is satisfactory for routine work. Aluminium and titanium interfere, probably by forming the corresponding potassium-metal fluorides. Various efforts to keep these metals in solution have not yet succeeded. If these components, however, occur in relatively small concentrations as in our material, they cause no major errors. Calcium, on the other hand, often occurs in large quantities and interferes in the presence of trivalent iron. When the iron is reduced quantitatively to the divalent state, this difficulty is removed, and silica can be determined even in iron ore containing large quantities of calcium.

ACKNOWLEDGEMENT

We wish to thank Dr. Y. SUNDSTRÖM for valuable criticism and helpful suggestions in the preparation of this paper.

SUMMARY

A rapid and reliable routine method for determination of silica in iron ore has been developed and tested. The silica is converted to potassium fluosilicate by digestion with hydrofluoric acid, hydrochloric acid and potassium chloride and determined volumetrically.

RÉSUMÉ

Une méthode de dosage rapide est proposée pour le dosage de la silice dans des minerais de fer. La silice est convertie en fluosilicate de potassium et dosée volumétriquement par l'hydroxyde de sodium.

ZUSAMMENFASSUNG

Beschreibung einer Schnellmethode zur Bestimmung von Kieselsäure in Eisenerzen. Die Kieselsäure wird in Kaliumfluorosilikat übergeführt und mit Natronlauge titriert.

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THE SEPARATION AND PHOTOMETRIC DETERMINATION OF CHROMIUM AND VANADIUM

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Methyl isobutyl ketone has been used widely in analytical chemistry for the extraction of chromium¹⁻⁴. There have been no quantitative studies reported of the extraction of hexavalent chromium in the presence of pentavalent vanadium, and it was the purpose of the present investigation to develop a rapid method for the separation and determination of chromium and vanadium.

APPARATUS AND REAGENTS

A Beckman Model DU spectrophotometer was used for all optical density measurements. It was equipped with 1-cm absorption cells. Extractions were made in 50-ml conical separatory funnels. The methyl isobutyl ketone (4-methyl-pentanone-2) was purchased from Coleman, Matheson and Bell, and from Eastman. It was distilled, and the fraction boiling between 114° and 116° was used for the extractions.

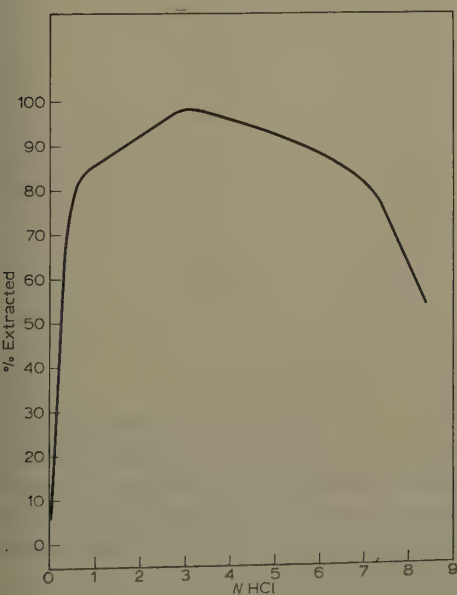


Fig. 1. The extraction of hexavalent chromium as a function of the aqueous hydrochloric acid concentration.

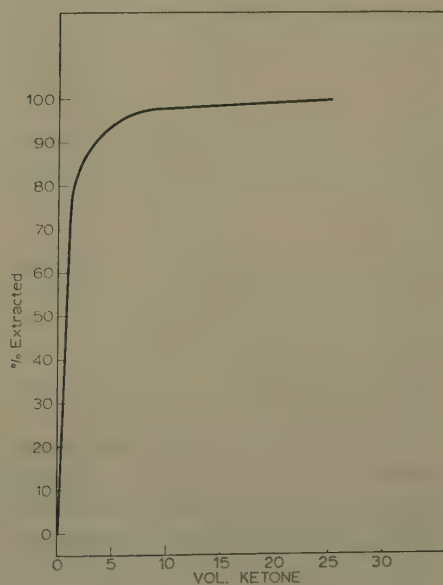


Fig. 2. The extraction of hexavalent chromium as a function of the volume of ketone.

EXPERIMENTAL

Extraction studies

Extraction studies were made on solutions of different acidities containing from 1–5 mg of hexavalent chromium using different amounts of solvent. 5-ml aliquots of potassium dichromate solutions of known chromium content were pipetted into

TABLE I

EXTRACTION OF HEXAVALENT CHROMIUM FROM 3 *N* HYDROCHLORIC ACID USING 25 ml OF METHYL ISOBUTYL KETONE

Chromium taken mg	Chromium found in ketone phase mg	Chromium found in aqueous phase mg	Amount extracted %
5.414	5.401	0.010	99.8
	5.376	0.033	99.3
4.873	4.872	0.006	100
	4.868	0.002	99.8
4.331	4.296	0.014	99.2
	4.329	0.010	100
3.790	3.789	0.000	100
	3.769	0.011	99.4
3.249	3.239	0.010	99.7
	3.248	0.003	100
2.707	2.686	0.012	99.2
	2.691	0.009	99.4
	2.689	0.013	99.4
2.166	2.152	0.013	99.4
	2.165	0.003	100
	2.158	0.010	99.6
1.624	1.614	0.010	99.4
	1.615	0.010	99.4
	1.620	0.005	99.8
1.083	1.078	0.004	99.5
	1.079	0.003	99.6
	1.074	0.006	99.4

separatory funnels, and increments of standard hydrochloric acid were added so that the acidities differed by 0.3 *N*. The solutions were diluted to a volume of 10 ml with water. The acid solutions were treated with a measured volume of methyl isobutyl ketone and shaken for 30 sec. The aqueous phase was separated and analyzed for chromium by a method suggested by WAGNER, HULL AND MARKLE⁵. The chromium was stripped from the ketone phase by washing with five 10-ml portions of water, and the washings were analyzed for chromium.

The results of this study, as shown in Figs. 1 and 2 and in Table I, indicate that the hexavalent chromium was quantitatively extracted when the aqueous phase was 3 *N* in hydrochloric acid, and the volume of ketone was 25 ml.

The distribution of pentavalent vanadium was studied by extracting 3 *N* hydrochloric acid solutions of ammonium vanadate containing from 5–25 mg of vanadium with 25 ml of methyl isobutyl ketone and determining the vanadium content of the aqueous phase. The results of this study, as listed in Table II, indicate that less than 1.5% of the vanadium was extracted under these conditions.

TABLE II
EXTRACTION OF PENTAVALENT VANADIUM FROM 3 *N* HYDROCHLORIC ACID USING 25 ml OF METHYL ISOBUTYL KETONE

Vanadium taken mg	Vanadium found in ketone phase mg (calc.)	Vanadium found in aqueous phase mg	Amount extracted %
24.975	0.162	24.813	0.65
	0.264	24.711	1.06
19.820	0.102	19.718	0.52
	0.144	19.676	0.73
15.336	0.091	15.245	0.59
	0.082	15.254	0.54
10.244	0.081	10.163	0.78
	0.090	10.154	0.88
8.713	0.077	8.636	0.88
	0.072	8.641	0.82
6.970	0.064	6.906	0.92
	0.070	6.900	1.00
5.244	0.058	5.186	1.10
	0.051	5.193	0.97
5.112	0.047	5.065	0.92
	0.051	5.061	0.99
3.496	0.041	3.455	1.17
	0.036	3.460	1.03
1.748	0.021	1.727	1.20
	0.024	1.724	1.37

Preparation of calibration curves

The absorption spectrum of hexavalent chromium extracted into methyl isobutyl ketone was studied in the 300- to 500- $m\mu$ range (Fig. 3). An absorption maximum was found at 444 $m\mu$. A plot of optical density against concentration at this wavelength gave a straight line with a slope of 3.41, and an extinction coefficient of 3.42 ± 0.07 ml/cm/mg was calculated from the data in Table III.

The work of SANTINI, HAZEL AND McNABB⁶ showed that the vanadyl ion is suitable for photometric analysis. Therefore, the absorption spectrum of ammonium vanadate saturated with methyl isobutyl ketone in 3 *N* hydrochloric acid and reduced with

TABLE III

OPTICAL DENSITIES OF VARIOUS AMOUNTS OF HEXAVALENT CHROMIUM IN 25 ml OF METHYL ISOBUTYL KETONE AT 444 m μ

Conc. Cr taken mg/ml	Optical density	$e = \text{optical density}/\text{conc.}$ ml/mg
0.2166	0.732	3.38
0.1949	0.655	3.35
0.1732	0.594	3.43
0.1516	0.512	3.38
0.1299	0.444	3.42
0.1083	0.368	3.39
0.0866	0.300	3.46
0.0649	0.220	3.39
0.0433	0.156	3.60

TABLE IV

OPTICAL DENSITIES OF VARIOUS AMOUNTS OF TETRAVALENT VANADIUM IN 3 *N* HYDROCHLORIC ACID SATURATED WITH METHYL ISOBUTYL KETONE AT 760 m μ

Conc. V taken mg/ml	Optical density	$e = \text{optical density}/\text{conc.}$ ml/mg
2.891	0.943	0.325
2.478	0.800	0.325
2.065	0.665	0.322
1.652	0.532	0.322
1.239	0.397	0.320
0.826	0.270	0.326
0.413	0.135	0.326

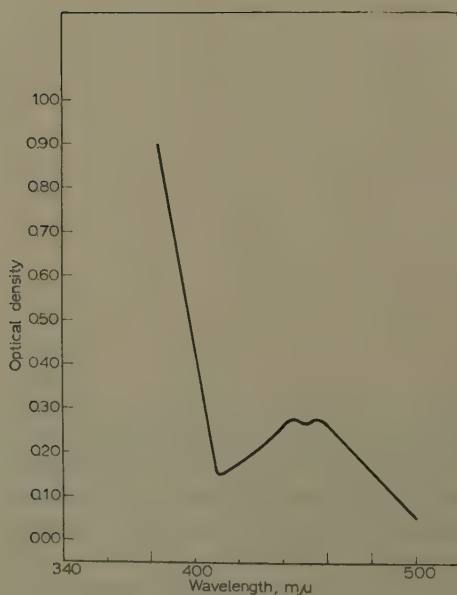


Fig. 3. The absorption spectrum of hexavalent chromium in the ketone phase.

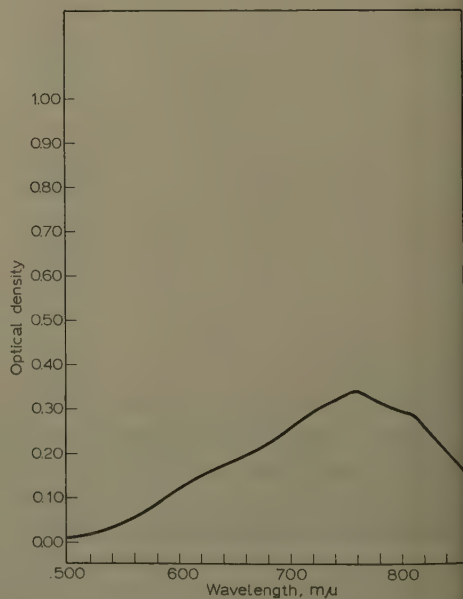


Fig. 4. The absorption spectrum of reduced vanadium in the aqueous phase.

sodium metabisulfite to vanadyl sulfate was studied in the 500- to 900-m μ range (Fig. 4). An absorption maximum was found to occur at 760 m μ . A plot of optical density against concentration gave a straight line with a slope of 0.324, and an extinction coefficient of 0.322 ml/cm/mg was calculated from the data in Table IV.

Color stability studies

In order to determine if any reduction occurred, as reported by HEILBORN⁷, a solution of potassium dichromate was acidified and extracted. Optical density measurements of the organic phase were made every 10 min for 3 h. These data, as shown in Fig. 5, revealed that there was no change in optical density during the first

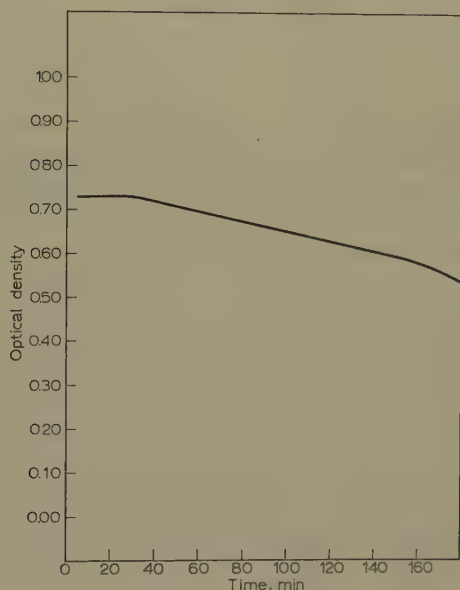


Fig. 5. Optical density of hexavalent chromium in the ketone phase as a function of time.

30 min. However, after 30 min, the optical density was found to decrease. It is apparent that these measurements must be made immediately after extraction.

A similar study was made of the reduced vanadium in the aqueous phase. It was found that the color was stable for 20 h.

Determination of chromium and vanadium in mixtures

Aliquots of standard solutions of potassium dichromate and ammonium vanadate were mixed, treated with 5 ml of 6 *N* hydrochloric acid, and brought to a volume of 10 ml with water. The acidic solutions were shaken for 30 sec with 25 ml of methyl isobutyl ketone. The optical density of the ketone phase was measured at 444 m μ , and the chromium content was calculated from this measurement.

The aqueous phase was treated with 0.5 g of sodium metabisulfite, and the solution was boiled for 10 min. This solution was cooled, transferred to a 10-ml volumetric

flask, and diluted to the mark with water. From the optical density measurement at 760 $m\mu$, the vanadium content was calculated. The results are given in Table V. The error noted in the table is of the order inherent in colorimetric methods.

TABLE V
RESULTS OF CHROMIUM AND VANADIUM DETERMINATIONS IN MIXTURES

<i>Cr taken</i> mg/ml	<i>V taken</i> mg/ml	<i>Cr found</i> mg/ml	<i>V found</i> mg/ml
0.49	0.00	0.47	0.00
0.49	1.02	0.47	1.04
0.49	2.05	0.47	2.10
0.24	2.05	0.25	2.07
0.00	2.05	0.00	2.06

Steel analysis

A 1-g sample of steel shavings (steel containing approximately 2.5% Cr and 1% V) was weighed out and transferred to a 250-ml beaker. The sample was treated with 20 ml of 3 *M* sulfuric acid and 4 ml of 6 *M* phosphoric acid. The mixture was heated until reaction ceased. 2 ml of concentrated nitric acid was added, and the solution was boiled until brown fumes were no longer expelled. The solution was diluted to approximately 50 ml, treated with 1 ml of 0.1 *M* silver nitrate and 5 ml of 20% potassium persulfate solution, and boiled until the color of permanganate was observed. 5 ml of 6 *M* hydrochloric acid was added to destroy this color. The solution was boiled until its volume was reduced to approximately 30 ml, neutralized with approximately 30 ml of 6 *N* sodium hydroxide, and filtered into a 100-ml volumetric

TABLE VI
RESULTS OF CHROMIUM AND VANADIUM DETERMINATIONS IN STEEL

<i>Cr reported</i> %	<i>V reported</i> %	<i>Cr found</i> %	<i>V found</i> %
3.52	0.97	3.55	0.96
		3.54	0.97
		3.54	0.96
0.95	0.18	0.94	0.12
		0.94	0.13
		0.94	0.13

flask. The precipitate was washed with two 10-ml portions of water. The washings were added to the flask, and the contents were diluted to the mark with water. A 5-ml aliquot of this solution was transferred to a separatory funnel and treated as described above. The results of two steel analyses are reported in Table VI. In the case of the second sample, better results would have been obtained with a 2-g sample.

SUMMARY

A study was made on the extraction of hexavalent chromium from hydrochloric acid solutions with methyl isobutyl ketone. Quantitative extraction was accomplished from 3 *N* hydrochloric

acid with 25 ml of solvent. Under these conditions, it was found that chromium could be extracted from vanadium. A procedure was developed for the colorimetric determination of chromium in the ketone phase and of vanadium in the aqueous phase. The analytical procedure was used to analyze standard steel samples for chromium and vanadium, and the results obtained by this method were found to agree with the accepted values.

RÉSUMÉ

Une étude a été effectuée sur l'extraction du chrome(VI), en solution chlorhydrique, au moyen de méthylisobutylcétone. Il est possible de séparer ainsi le chrome du vanadium. Une méthode colorimétrique est décrite pour le dosage de ces deux éléments, en particulier dans les aciers.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Trennung von Chrom(VI) und Vanadium durch Extraktion mit Methylisobutylketon mit anschliessender colorimetrischer Bestimmung der beiden Elemente.

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Anal. Chim. Acta, 25 (1961) 193-199

A NEW SPECIFIC TEST FOR ALUMINIUM

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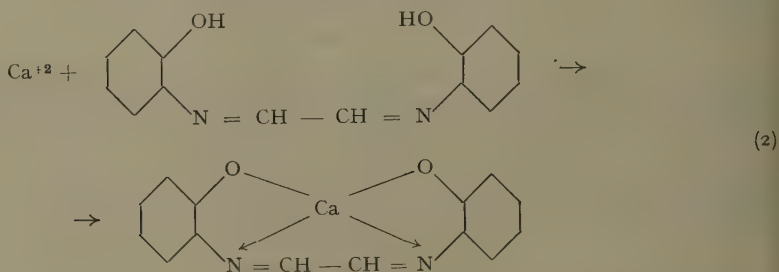
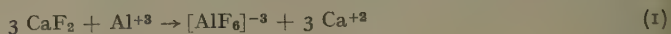
(Received January 27th, 1961)

It has been shown by FEIGL¹ that "demasking" reactions can be successfully used for the sensitive detection of materials, by causing the formation of new, more stable complexes through the liberation of previously "masked" ionic species. The demasking reactions of ferrocyanide², yellow palladium dimethylglyoxime complex³ and zirconium alizarinate⁴ have been used for the detection of mercury(II), cyanide and fluoride respectively.

The present paper provides a new example of how differences in the stability of colourless inorganic complexes may be indicated by colour tests and utilized for analytical purposes.

From insoluble calcium fluoride, calcium ions are liberated by the addition of aluminium ions, owing to the formation of the highly stable $[\text{AlF}_6]^{-3}$ complex. The subsequent detection of calcium ions by the recently reported specific method of

GOLDSTEIN AND STARK-MAYER⁵ makes possible a new specific test for aluminium, *i.e.*:



As the displacement of calcium (eqn. 1) was found to be restricted to aluminium among a series of ions tested under certain conditions, and as the formation of the inner complex of calcium with glyoxal bis(2-hydroxyanil) (eqn. 2) has been shown to form a basis for a strictly specific test for calcium, the above process is recommended as a reliable and specific method for the detection of aluminium.

EXPERIMENTAL

Materials

Glyoxal bis(2-hydroxyanil) was prepared by BAYER's method⁶: 4.4 g of *o*-aminophenol were dissolved in 1 l of water at 80° and 3.0 g of 40% aqueous solution of glyoxal was added. The mixture was kept at 80° for 30 min and then for 12 h in an ice box. The precipitate was filtered, washed with water and recrystallized from methanol. A 1% alcoholic solution of the reagent was used. All the other materials used were of analytical grade.

General procedure

A few mg of pure calcium fluoride were placed in a micro test tube, and a drop of the neutral or slightly acidic test solution was added followed by a few drops of the reagent solution and one drop of 10% sodium hydroxide and 10% sodium carbonate solution. The precipitate formed was extracted with a few drops of chloroform. The presence of aluminium was indicated by the appearance of a red colour in the organic layer. (A blank test should be carried out for comparison).

Identification limit: 0.5 μg Al.
Dilution limit: 1 : 100,000.

Interferences

The presence of a relatively large amount of any of the following ions does not interfere with the test: Na, K, Mg, Sr, Ba, ZrO, Cr, Mn, Fe, Co, Ni, Mo, W, Re, Ru, Rh, Pt, Cu, Ag, Au, Zn, Hg, B, Ga, Tl, Ge, Sn, Pb, As, Sb, Bi, U, Ce.

In view of the similar displacing effects on calcium fluoride of both beryllium and aluminium, the test should be carried out in tartaric acid solution, which forms a stable complex with beryllium.

It has been found by previous workers that cadmium also reacts with the reagent

under similar conditions to calcium, and the blue product obtained is extractable with chloroform. This interference may, however, be eliminated⁵ if a 10% sodium cyanide solution is introduced in addition to the 10% sodium hydroxide solution as described in the general procedure.

Calcium ions obviously interfere with the test, but this difficulty may be overcome by the precipitation of calcium as the oxalate, followed by filtration.

It should be pointed out that the test solution must be neutral or slightly acidic. If the pH of the test solution is less than 2, calcium ions are liberated from the fluoride. On the other hand, if the pH of the solution exceeds 8, the demasking of calcium by aluminium does not occur.

SUMMARY

A new specific spot test for aluminium is described. The test is based on the demasking action of aluminium ion on calcium fluoride, and subsequent detection of the liberated calcium by glyoxal bis-(2-hydroxyanil).

RÉSUMÉ

Une nouvelle réaction à la touche, spécifique, est décrite pour l'identification de l'aluminium. On utilise comme réactif le fluorure de calcium; l'aluminium se complexant avec le fluorure, le calcium est libéré et peut réagir avec le bis-(hydroxy-2-anil)-glyoxal.

ZUSAMMENFASSUNG

Beschreibung einer neuen, spezifischen Nachweisreaktion (Tüpfelprobe) für Aluminium durch Komplexbildung mit Calciumfluorid und Nachweis des dabei in Freiheit gesetzten Calciums mit Bis-(2-hydroxyanil)-glyoxal.

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Anal. Chim. Acta, 25 (1961) 199-201

Short Communications

Applications de la chélatométrie XIV. Dosage volumétrique des vic-dicétones

Nous avons montré, en collaboration avec MERLIN¹ que le diacétyl, premier terme des vic-dicétones, pouvait être dosé par chélatométrie: après réaction avec le chlorhydrate d'hydroxylamine en présence d'acétate de sodium et d'acétate de nickel, le diacétyl est complètement précipité sous forme de diméthylglyoximate de nickel et il suffit de titrer le nickel en excès après filtration; on emploie pour cela l'acide éthylène-diaminotétracétique en milieu ammoniacal et la murexide comme indicateur.

Utilisant le même mode de précipitation des dioximates de nickel nous avons

ensuite, en collaboration avec VIEILLET², montré la possibilité de doser, toujours par chélatométrie, quelques *vic*-dioximes d'emploi fréquent en analyse minérale.

Dans le premier travail¹ nous avons émis la supposition que la méthode décrite pourrait être employée pour les homologues supérieurs du diacétyl; la présente communication a pour but de rapporter les essais que nous avons effectués sur quelques uns de ces produits. La seule modification apportée dans le processus opératoire consiste dans un retard que nous avons observé pour l'introduction de l'acétate de nickel; en même temps que l'échantillon pesé et le chlorhydrate d'hydroxylamine *N*,

TABLEAU I

Produit essayé	Poids mg	Titre trouvé	Déviati %
2,3-pentane dione	513	98.8	— 1.2
	521	99.2	— 0.8
	527	98.7	— 1.3
	509	99.0	— 1.0
2,3-pentane dione + diéthylcétone 75:25	681	74.3	— 0.9
	672	74.3	— 0.9
	609	74.2	— 1.1
2,3-pentane dione + diéthylcétone 50:50	802	49.3	— 1.4
	823	49.5	— 1.0
	837	49.3	— 1.4
1-phényl 1,2-propane dione	708	98.2	— 1.8
	717	98.5	— 1.5
	723	98.3	— 1.7
1,2-cyclohexane dione	502	98.8	— 1.2
	523	98.9	— 1.1
	549	99.1	— 0.9
1-méthyl 2,3-cyclohexane dione	608	98.4	— 1.6
	581	98.2	— 1.8
	597	98.5	— 1.5

nous avons introduit 10 ml d'une solution aqueuse d'acétate de sodium $\text{CH}_3\text{COONa} \cdot 3 \text{H}_2\text{O}$ à 410 g/l; 25 ml d'une solution aqueuse d'acétate de nickel $(\text{CH}_3\text{COO})_2\text{Ni} \cdot 4 \text{H}_2\text{O}$ à 50 g/l ont été introduits seulement après trois heures d'ébullition, soit donc une heure avant la fin du traitement. Cette modification n'a d'autre but que de faciliter l'oximation en travaillant dans un milieu plus riche en alcool et donc meilleur solvant.

Le Tableau I résume les résultats que nous avons obtenus.

Seraincourt, Seine et Oise (France)

C. HENNART

¹ C. HENNART ET E. MERLIN, *Chim. anal.*, 41 (1959) 287.

² C. HENNART ET F. VIEILLET, *Anal. Chim. Acta*, 25 (1961) 150.

Reçu le 24 janvier, 1961

Potentiometric titration of thallium(III) with chromium(II) solution

Recently certain methods for the determination of thallium(III) based on reductimetric titration with titanium(III) and ascorbic acid have been studied in these laboratories; although the reactions are quantitative, they are rather sluggish in dilute solutions near the end-point. Titration with chromium(II) solution was therefore examined.

Chromium(II) solutions are the strongest reductimetric titrants used, as indicated by the standard redox potential¹ -0.41 vs. the normal hydrogen potential; they therefore have certain advantages over other reagents such as titanium(III)². Although the reduction is smooth even at room temperature with chromium(II) solutions, great care must be taken to protect the titrant from atmospheric oxidation and to prepare it from pure compounds³. Difficulties involved with visual indicators for the end-point were eliminated by using a potentiometric titration. Irreversible indicators such as methyl orange were examined but it was necessary to apply an indicator correction. The potentiometric method was found to be generally more satisfactory.

An approximately (0.05 *N*) chromium(II) solution was prepared by the reduction of A.R. potassium dichromate by hydrogen peroxide and amalgamated zinc⁴, the overall acid concentration being about 2–3 *N*, and the solution was stored in an automatic burette. A standard (0.05 *M*) thallium(III) solution was prepared by dissolving the required amount of thallic oxide (Spec-pure) in concentrated sulphuric acid and then diluting to a definite volume. The chromium(II) solution was standardised against iron(III) solution while the strength of the thallium(III) solution was checked iodometrically.

The titrations were performed in a three-necked flask holding the carbon dioxide tube, platinum electrode and an agar-agar bridge connected to an external calomel electrode; a Doran pH meter (Universal Model No. 4981) was used for *E* measurement.

For a determination, an aliquot of thallium(III) solution was treated with bromine⁵ to ensure that all the thallium was present in the trivalent state. The titrations were performed at an acid concentration of 2–3 *N* in an atmosphere of oxygen-free carbon dioxide, the end-point being indicated by a fall in *E* of the order of 110–130 mV. The temperature of the titration was 30–35°. The results of determinations of thallium(III) at varying concentrations are shown in Table I.

TABLE I
DETERMINATION OF THALLIUM(III)

Thallium(III) taken in 20 ml soln. (mg)	Chromium(II) added (ml)	Thallium(III) found (mg)	% deviation
100.00	19.63	100.11	0.11
110.60	21.70	110.67	0.06
115.60	22.70	115.77	0.14
125.00	24.70	125.97	0.77

When methyl orange (2 drops of a 1% solution) was used as indicator, the same preoxidation, acidity and inert atmosphere were used as for the potentiometric titration. The end-point was indicated by irreversible bleaching of the pink colour of the indicator. The results obtained were slightly higher than those obtained by the potentiometric method, unless an indicator blank was determined and deducted.

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RITA MAJUMDAR
M. L. BHATNAGAR

¹ G. GRAUBE AND G. BRINTZINGER, *Z. Elektrochem.*, 33 (1927) 112.

² R. PALLAUD, *Chim. anal.*, 33 (1951) 181.

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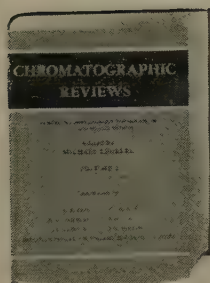
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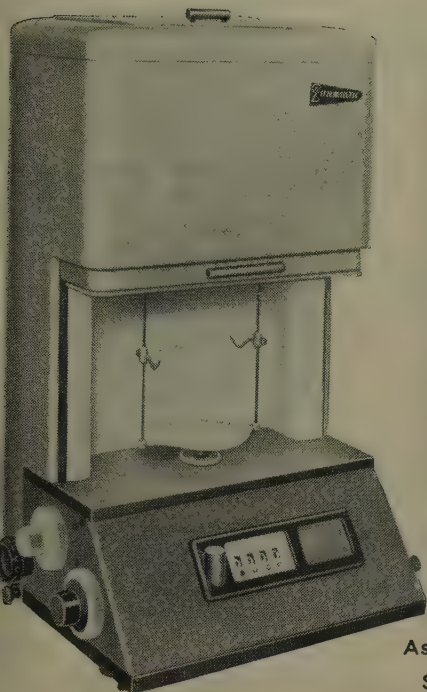
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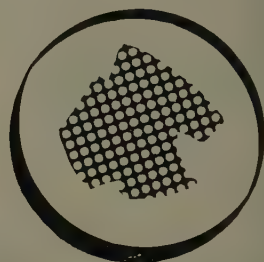
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